Geochimica et Cosmochimica Acta

JOURNAL OF THE GEOCHEMICAL SOCIETY

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Four issues per volume, three volumes per year

Subscription *per annum* (including postage) (A) £21 (U.S.A. $60.00); (B) For individual subscribers who write directly to the publisher certifying that the Journal is for their private use, £7.7s. (U.S.A. $21.50). Members of the Geochemical Society, or non-members who occasionally publish papers in the Journal, £3. 11s. 6d. (U.S.A. $10.00) *per annum.*

Back numbers, £10 (U.S.A. $28.00) per volume

Single issues, £2. 10s. (U.S.A. $7.00) each

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HEADINGTON HILL HALL, OXFORD 122 EAST 55TH STREET, NEW YORK 22, N.Y.

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Geochimica et Cosmochimica Acta, 1961, Vol. 25, pp. 1 to 13. Pergamon Press Ltd. Printed in Northern Ireland

5856-29A

Silicon in the metal phase of enstatite chondrites and some geochemical implications

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(*Received* 15 *January* 1961)

Abstract—Some recent hypotheses have proposed that silicon occurs as a major component of the earth's core. Since the chemical evolution of the earth may have been analogous in some respects to that which occurred in meteorites, a search for silicon was made in the metal phases of chondrites. Using X-ray and chemical methods, it was established that between 2 and 6 atomic per cent of silicon occurred in solid solution in the metal phases of all eight enstatite chondrites which were examined. No silicon was found in the metal phase of ordinary chondrites.

Evidence relating to the possible occurrence of silicon in the earth's core is reviewed, and the significance of the new meteoritic data in relation to this hypothesis is discussed in some detail.

A study of the conditions which accompany the segregation of a core, both in the earth and in the parent meteoritic body, lead to the conclusion that the core is unlikely to be in chemical equilibrium with the surrounding mantle. One of the principal effects of this disequilibrium is the diffusion of silicon from the core into the adjacent region of the mantle, resulting in the reduction of oxidized iron and precipitation of metallic iron. This effect may be responsible for the anomalous seismic velocity gradients which are observed in the bottom 200 km of the mantle. This region is likely to be mechanically unstable, owing to the tendency of precipitated iron to collect and sink into the core.

Owing to inhomogenieties in ionic and electronic transport properties in this region, attainment of chemical equilibrium across the core–mantle boundary is accompanied by generation of electric currents. These may be relevant to the origin of the earth's magnetic field, and may also affect the electromagnetic coupling between core and mantle.

1. Introduction

The suggestion that silicon occurs as a major component of the earth's core was independently made by Ringwood (1958, 1959), and MacDonald and Knopoff (1958). One of the chief supporting arguments for this view was based upon the chemical compositions of chondritic meteorites. The authors cited above found that it was impossible to construct a satisfactory earth model from material of chondritic composition without removing some silica from the silicate phase and transferring it to the metal phase in the form of elemental silicon. Since chemical compositions of chondrites play such an important part in the argument, it appeared desirable to make a search for silicon in the metal phases of chondrites.

Oxidation–reduction equilibria among the minerals of chondrites have recently been studied by Ringwood (1961). An extreme range in oxidation states is found. It seemed that the highly reduced enstatite chondrites would be the most promising to investigate. These contain reduced chromium, calcium, and phosphorus minerals, and the silicate phases do not contain oxidized iron. All other chondrites contain appreciable quantities of FeO in the silicate phase. Thermodynamic considerations show that metal which contains reduced silicon is unlikely to co-exist in equilibrium with silicates containing substantial amounts of FeO.

A preliminary account of some of the experimental data discussed in this paper has been published (Ringwood, 1960a).

2. Experimental

(a) *X-ray investigation*

Small samples of the following enstatite chondrites were obtained—Pillistfer, Indarch, Hvittis, Saint Marks, Daniels Kuil, Saint Sauveur, Blithfield and Khairpur. They were crushed and the metallic phase was separated magnetically. The −150 mesh magnetic fraction was then examined by X-ray diffraction using an 11-cm powder camera, and Co radiation. In each sample, kamacite was the only metal phase observed. The lattice parameters of the kamacites were determined, and are set out in Table 1.

The metal phases of a number of ordinary chondrites were similarly examined. All specimens contained varying proportions of both kamacite and taenite. The back diffraction lines of most kamacites were too diffuse to allow accurate determination of the lattice parameters. Five samples, however, i.e. Felix, Homestead, Knyahinya, Lance and Warrenton, were sufficiently distinct to permit measurement. They fell in the range 2·8682 ± 0·0005 Å. This corresponds to an average of 5 ± 1 per cent of nickel in solid solution (Owen and Burns, 1939). The latter authors found that the kamacite lattice parameters from fifteen meteoritic irons (octahedrites) were within the range 2·8686 ± 0·00015 Å. This indicates the presence of about 6 per cent of nickel.

In Table 1, it is observed that the lattice parameters of kamacite from all the enstatite chondrites examined are significantly lower than those of kamacite from ordinary chondrites and irons. Furthermore they are *lower* than that of pure iron. Chemical analysis shows that these kamacites contain between 4·5 and 8·4 per cent of nickel in solid solution, which *increases* the lattice parameter of pure iron. The abnormally low parameters of enstatite chondrite kamacites must therefore indicate the presence of some other element in solid solution, which causes a contraction.

A process of elimination leads to the conclusion that the additional component is probably silicon. This is the only element which forms extensive solid solutions with iron, causing marked contraction of the lattice parameter, and at the same time, occurs in sufficient quantities in chondrites to produce the observed contraction. A literature survey revealed that 2 (atomic) per cent of silicon had previously been recorded in the metal phase of Blithfield (Johnston and O'Connor, 1922). Furthermore in the metal phases of the enstatite chondrites Khairpur and Daniels Kuil (Prior, 1916) and Saint Marks (Klein, 1906), the analysts have commented upon an apparent "excess" of SiO_2, but could not account for its origin. These results thus support the conclusion drawn above.

Farquhar *et al.* (1945) have determined the lattice parameters of pure iron–silicon solid solutions as a function of composition. Using Owen and Burn's (1939) data, it is possible to determine what the lattice parameter of the kamacite would be, if it consisted only of iron and nickel. The contraction (ΔÅ), due to the silicon, is obtained by subtracting the observed lattice parameter from the value for the corresponding pure Fe–Ni alloy. If it is assumed that the relative contraction due to the solution of silicon in α-iron is not affected by the presence of up to 8·4 per cent Ni in solid solution, we may estimate the silicon content of kamacites by comparing the observed contractions with those occurring in pure Fe–Si solid solutions of known composition. The estimated values range from 5 to 10·5 atomic per cent silicon (Table 1).

Table 1. Some properties of kamacite from enstatite chondrites and other meteorites

Reference	Meteorite	Atoms % Ni	Observed lattice parameter (Å)	ΔÅ Contraction due to solid solution of Si (Å × 10^4)	Atoms % silicon in solid solution in kamacite		Weight % insoluble residue	Weight % soluble silicon in pure silicate fraction
					X-ray	Chemical analysis*		
1	Indarch	6·7	2·8619	68	10·5	5·6	5·1	0·6
2	Saint Marks	6·4	2·8630	56	9·0	5·3	2·6	0·7
3	Saint Sauveur	4·5	2·8632	48	8·0	4·0	<1	
4	Daniels Kuil	6·2	2·8655	30	5·0	3·6	—	
5	Hvittis	7·6	2·8655	35	5·5	3·6	<1	
6	Khairpur	7·0	2·8652	36	5·5	3·5	3·0	0·3
7	Pillistfer	8·4	2·8652	40	6·5	2·4	1·0	0·4
8	Blithfield	6·4	2·8659	27	5·0	2·0	<1	0·9
9	Kamacite from 5 ordinary chondrites	Average 5	2·8682 ±0·0005					
10	Kamacite from 15 iron meteorites	6·2	2·8686 ±0·00015					
	Pure Iron		2·8665					

* Corrected for soluble silicon derived from silicate inclusions in the metal.

References

1. Wiik (1956).
2. Cohen (1906)
3. Lacroix (1923).
4, 6. Prior (1916).
5. Borgstrom (1903).
7. Lacroix (1905).
8. Johnston and Connor (1922).
9. Ringwood (1961).
10. Owen and Burns (1939).

(b) *Chemical investigation*

It appeared most desirable to confirm the conclusions derived from the X-ray work by direct chemical analysis. Determination of silicon in the metal phase of stone meteorites meets with difficulties because of the danger of contamination of mechanically separated samples of metal phase by silicates. An additional difficulty was raised by the small amount of samples available—apart from Pillistfer (20 g) they varied between 2 and 0·2 g.

The first step was mechanically to separate from the parent meteorite, the purest possible sample of metal phase. This task was carried out with great skill and care by Mr. R. Rudowski, to whom the author is considerably indebted.

Samples were crushed and the magnetic fraction was separated by hand magnet, thus providing a product rich in metal, but containing a moderate amount of silicate impurity. This sample was then ground for several hours in an agate mortar under acetone. At intervals, a magnetic separation was carried out on the sample, and the non-magnetics were discarded. When a stage was reached at which further grinding did not produce any non-magnetic fraction, the operation was stopped. Microscopic examination of the sample at this stage did not reveal any silicates on the surfaces of the flattened metallic flakes. However, it was still possible that some of the flakes could contain small silicate inclusions.

The samples (apart from Hvittis and Daniels Kuil, which were insufficient in quantity) were next classified according to density on a superpanner. This enabled less dense grains containing silicate inclusions to be largely eliminated. The cleanest fraction from the superpanner was then selected for chemical analysis. The coarse sample from Pillistfer was further cleaned by repeated fusion with sodium hydroxide, followed by thorough washing.

Optical examination showed that the silicates of the enstatite chondrites investigated consisted almost entirely of iron-free enstatite. Olivine, if present, amounted to less than 2 per cent of the total. The procedure adopted was to dissolve the metal phase in dilute acid, under such conditions that any enstatite inclusions in the metal were unaffected. The dilute acid used was strong enough to attack any forsterite present—however, this formed such a small proportion of the total silicate, which itself formed, at the most, only a few per cent of the metal phase (Table 2), that it is unable to make a significant contribution to the silicon determined in the metal.

This latter point was checked by using exactly the same chemical procedures to carry out silicon determinations on pure samples of silicates, which were obtained during magnetic separation (Table 1). The amounts of dissolved silicon were, with the exception of Blithfield, much less than those found in the accompanying metal phases. Since the amount of silicate residue after the metal had been dissolved was known, it was possible to correct the metal analyses for silicon which might have been derived from silicate inclusions. All of the corrections were very small.

Chemical analyses of the metal phases were carried out by Mr. J. Easton of the Australian National University. About 50 mg of the sample was dissolved in a mixture of dilute (3·6 per cent v/v) sulphuric and (9 per cent v/v) nitric acids. The solution was then centrifuged from any undissolved residue, which was dried and weighed. After reduction, silicon was estimated as the blue silicomolybdic acid.

Relative deviation of the method performed on several standard iron–silicon alloys was 2·5 per cent. The results are set out in Table 1.

Some further work was carried out on metal from Pillistfer, as a check on these results. Silicon was determined gravimetrically on a $\frac{1}{2}$-g sample, yielding a result identical with the colorimetric estimation. Magnesium was determined both by atomic absorption, and colorimetric methods by Mr. E. Davis of the Chemical Research Laboratories, C.S.I.R.O. Phosphorus was also determined.* Magnesium was found to average 0·09 per cent, whilst phosphorus amounted to 0·10 per cent. These low magnesium results show conclusively that an insignificant amount of included silicates were dissolved during solution of the metal phase. The low phosphorus content disposes of the remote possibility that the observed lattice parameter contraction of the kamacite could be due to solid solution of phosphorus.

(c) *Discussion*

The silicon contents of the metal phases of enstatite chondrites determined by both X-ray and chemical methods are compared in Table 1. It is observed that there is good qualitative agreement between the two methods. However, the X-ray methods yield values which are about twice as high as the chemical determinations.

The major uncertainty in the X-ray determinations lies in the fact that the lattice parameter variation of Fe–Si solid solutions is anomalous, consisting of two straight line segments which have very different slopes (Farquhar *et al.*, 1945). The discontinuity in slope lies at 10 atomic per cent Si. It is possible that the presence of some nickel in solid solution might alter the position of this discontinuity, and perhaps, also the slope of the curves. This may provide at least a partial explanation for the discrepancy. The detailed results on Pillistfer suggests that the chemical determinations are probably the more reliable.† The X-ray method nevertheless provides a very useful qualitative indicator for the presence of silicon.

3. Silicon in the Earth's Core

In the previous section we concluded that the metal phases from enstatite chondrites contain between 2 and 6 atomic per cent of silicon in solid solution. This has a bearing on a hypothesis advanced by Ringwood (1958, 1959), MacDonald and Knopoff (1958), and MacDonald (1959) which maintains that the earth's core contains silicon as a major component.

Arguments used by the above authors in supporting this hypothesis may be summarized.

(a) *Characteristic atomic number*

Experimental data on the relationship between density and pressure in the range 0–10^5 bars is available for many elements. Above 10^8 bars, the density of matter as a function of pressure and atomic number can be calculated by the Thomas–Fermi

* Davis also determined silicon by a different colorimetric method to that used by Easton, finding 1·3 wt per cent, compared to 1·2 per cent by Easton.

† Fredriksson (personal communication) has suggested that a second α_2 kamacite phase, not containing silicon, might be present in some of these chondrites. If correct, this might reconcile the results obtained by the two methods. The back diffraction lines of the α_2 phase (kamacitic) are diffuse, and it is difficult to identify on an X-ray photograph which has normal α lines.

method. Knopoff and Uffen (1954) have used the Birch–Murnaghan theory of finite strain to interpolate in the region between 10^5 and 10^8 bars. Fitting the inferred density of the outer core to their equation of state, they conclude that the representative atomic number (Z) of the outer core is 22. This is significantly less than that of iron ($Z = 26$). More direct support for this estimate has been published by Knopoff and MacDonald (1960) using an equation of state based on shock wave results covering pressures up to 4 Mbars.

This evidence indicates that the earth's core may contain substantial quantities of an element with a much smaller density than iron.

(b) *Density*

Comparisons of the density of the core, and the probable density of iron at high pressures (Birch, 1952; Bullard, 1953, 1957) indicate that the material of the core is somewhat less dense than would be expected for iron under similar pressure–temperature conditions. Birch points out that the discrepancy may be between 10 and 20 per cent. Support for this view has recently been provided by Knopoff and MacDonald (1960) using shock wave data on the density of iron, covering a range up to 4 Mbars. They concluded that the core is about 15 per cent less dense than iron under similar P–T conditions. Clearly, therefore, the core must contain a relatively light element, which can reduce the density of iron.

(c) *Elasticity*

Birch (1952) has drawn attention to a large discrepancy between the elastic ratio, K/ρ (K = incompressibility, ρ = density) of the core, and the probable elastic ratio of iron under similar conditions. The elastic ratio for the core just inside the core-mantle boundary, derived directly from seismic velocities, is 66 $(\text{km/sec})^2$. For iron at the same pressure, Birch estimates K/ρ to be 54·4 $(\text{km/sec})^2$. At the temperature of the core–mantle boundary, and allowing for melting and the presence of nickel, this would be reduced to at least 50 $(\text{km/sec})^2$ and would probably be closer to 45 $(\text{km/sec})^2$.

The preceding discussions indicated that the core probably contains in addition to iron–nickel, substantial amounts of an element with a low atomic number, low density, and which can increase the elastic ratio of iron by about 30 to 50 per cent. Limitations upon possible choices are imposed by the condition that this element must be reasonably abundant, miscible with liquid iron, and possess chemical properties which would allow it to enter the core.

Elements which have been considered in this respect by various authors are H, He, C, O, N, Mg, Si and S. We may reject H, He, C, O and N, since they are known to form interstitial solid solutions with iron. Additions of these elements do not significantly decrease the density of iron, since they occupy holes already present in the lattice. Magnesium is unlikely to be present in substantial amounts since it has a much greater affinity for oxygen than has silicon. Accordingly, any chemical conditions which may have led towards the incorporation of magnesium in the core would inevitably have caused the incorporation of much larger amounts of silicon.

This leaves us with silicon and sulphur as possibilities. It would require at least

14 per cent of sulphur to account for the required lowering of density.* 30 per cent to account for the characteristic atomic number, and about 50 per cent to produce the required increase in the elastic ratio.*

It appears improbable that the core would contain as much sulphur as this. Iron meteorites, which probably provide the most relevant indication, contain on the average, less than $\frac{1}{2}$ per cent of sulphur. In chondrites, the ratio S/(S + Fe + Ni) is only 7·5 per cent. Since the earth has probably been subjected to more intense reducing conditions at higher temperatures than chondrites (Ringwood, 1960b) and sulphur is volatile under these conditions (as CS_2, COS and H_2S), it is probable that the earth has lost sulphur relative to chondrites during the period of its formation.

A process of elimination thus points towards silicon as the most likely extra component of the earth's core. It possesses a low atomic number (14) and forms extensive substitutional solid solutions with iron, causing a marked reduction in density. Furthermore the elastic ratio of silicon is twice that of iron. Silicon also satisfies the criteria of abundance, miscibility with liquid iron, and chemical compatibility. After the oxides of iron and nickel, silicon dioxide is the easiest common oxide to reduce to the metal. The chemical conditions required for this reduction are well known and probably occurred during the earth's formation (Ringwood, 1959, 1960b).

(d) *Comparison between chemical composition of chondrites and the earth*

The hypothesis that the earth and chondrites possess similar chemical compositions† is attractive to many geochemists and cosmologists. The silicate phase of the average chondrite appears to contain more iron oxide than the earth's mantle. If chondrites are reduced to an FeO/MgO ratio similar to that probably occurring in the mantle, then the composition of the silicate phase of chondrites is close to that of a pyroxenite. There are many grounds for believing that minerals of olivine composition are more abundant in the mantle than pyroxenes. There is, therefore, too much SiO_2 in the silicate phase of chondrites to provide a satisfactory earth model. If the overall compositions of earth and chondrites are to be similar, the silicon from the excess SiO_2 must occur in the core. Detailed calculations (Ringwood, 1959) show that a satisfactory earth model based upon a chondrite composition requires the presence of about 20 per cent of silicon in the core. MacDonald and Knopoff (1958) and MacDonald (1959) have reached a similar conclusion using analogous arguments.

(e) *Silicon in the metal phase of enstatite chondrites*

The discovery of silicon in the kamacite of enstatite chondrites provides further support to the above views. It shows that chemical conditions during the formation of metal in meteorites were such as to allow silicon to collect with the metal. A more detailed discussion of the implications of this occurrence follows in the next section.

* The relevant estimates have been made using the density and elastic ratio of pyrite as an indication of the effect of sulphur on the properties of iron. Pyrite was chosen because it is a close packed structure containing sulphur atoms linked to iron atoms by partial metallic bonding.

† The hypothesis applied only to elements which are not volatile under high temperature reducing conditions. There is room for substantial differences in abundances of volatile elements, such as O, K, Rb, Cs, Pb, Tl, Bi and S, since the earth has probably been subjected to more intense high-temperature reduction than chondrites, and may be depleted in these elements.

4. Some Genetic Implications

Oxidation–reduction equilibria which have governed the chemical evolution of chondrites have been studied by the author (Ringwood, 1961). These studies suggest that the metal phase in chondrites has been produced *in situ* when primitive material of carbonaceous chondrite composition has been heated. The carbon reacted with oxidized iron to produce a metal phase. The extent to which the reaction proceeded depended principally upon the energy available, the temperature and the amount of carbon present. Variations in these factors have led to a continuous variation in the state of oxidation between primitive carbonaceous chondrites, in which all the iron is oxidized, and enstatite chondrites, in which all the iron is reduced, and which contain, in addition, reduced compounds of chromium, calcium and phosphorus.

The occurrence of silicon in the metal phase of enstatite chondrites is simply explained by this mechanism. After the oxides of iron and nickel, silicon dioxide is the easiest common oxide to reduce to the metal. For this reason, appreciable amounts of silicon are found in blast furnace irons. The reduction process in enstatite chondrites has been sufficiently intense to reduce some silicon, as well as all the iron and nickel.

In the case of the earth, the estimated silicon content of the core is about 20 weight per cent. This implies a higher degree of reduction of the silicate phase. Reduction must therefore have occurred at a higher temperature and a larger energy source must have been available. Thus, the thermal evolution of meteorites and of the earth has differed significantly. The question has been discussed by the author in papers previously cited. The energy sources available during chondrite formation were insufficient to permit complete melting and differentiation. Thus, the metal in chondrites is *in situ*, and in equilibrium. However, in the earth, the enormous gravitational energy dissipated during accretion has led to a very high average temperature of reduction, followed by complete melting, so that evidence of former local chemical inhomogeniety has been destroyed. The high concentration of silicon inferred in the earth's core is a consequence of these conditions.

MacDonald and Knopoff (1958) have suggested that the occurrence of silicon in the earth's core is the result of "squeezing" fayalite under the extreme pressures in the deep interior, so that the iron and silicon enter the core. The author is unable to visualize this process. Apparently the mantle is regarded as a semipermeable membrane, through which oxygen from the squeezed fayalite is able to escape freely. The squeezing mechanism is unable to explain the occurrence of silicon in the metal from enstatite chondrites, which formed under a relatively low pressure.

5. Disequilibrium between Core and Mantle

The basic similarity between metal formation in the blast furnace and formation of metal in meteorites and in the earth's core has been mentioned in a preceding section, and discussed in papers previously cited. It is desirable to explore further aspects of this relationship.

In a blast furnace, the iron is first produced by reduction at a high level and at a comparatively low temperature ($\sim$900°C) whilst the charge is still solid. As the charge gradually moves down the furnace, temperature increases, and melting

commences. The initial reduction of metal high in the furnace involves an equilibrium in which various components such as C, P, N, S, Si, Ti, Mn, Cr and V are partitioned between metal and silicates. After melting, the metal collects into drops which commence to sink through the slag into deeper and hotter regions of the furnace. The increasing temperature causes marked changes in the partition equilibria involving the components mentioned above. Equilibrium can be maintained only by a diffusion process across the metal slag interface. This is a slow process compared to the rate of sinking of the metal drops into hotter regions. The net result is that the drops are unable to maintain equilibrium with the slag through which they are sinking, and hence the metal which collects at the floor of a blast furnace is not in chemical equilibrium with the slag above (Hatch and Chipman, 1949). This behaviour has some obvious applications to meteorites and to the earth.

Very wide variations in the degree of reduction occur among chondrites. However, the metal in individual chondrites is in equilibrium with the surrounding silicates. This corresponds to the initial stage of reduction in a blast furnace. Let us suppose that all the chondrites from the parent meteoritic planet had been thoroughly melted, allowing the metal to segregate and form a core. Metal, containing nickel ranging from 5 to 70 per cent, phosphorus from 0 to 0·5 per cent, silicon from 0 to 3·0 per cent and various minor components such as Cr and C, would collect into masses which would sink rapidly through the meteoritic mantle into hotter zones where the equilibria are displaced. The suggested metallic core would become homogenized by convection, and little trace of the former extreme chemical inhomogeneity would remain. The mantle would similarly become homogenized. However, the core would now be out of chemical equilibrium with the mantle, and chemical reactions involving partition of minor components would proceed at the interface. In fact, this has happened to some extent in iron meteorites, which contain small quantities of C, Cr and P, which would not be in equilibrium with the average chondritic silicate containing 12 per cent FeO.

In the earth, the factors which would lead to disequilibrium between core and mantle are more cogent and numerous than for meteorites.

(a) It is likely that the initial oxidation states in the accreted earth, prior to melting, cover a much wider range than chondrites (Ringwood, 1960b). All gradations between completely oxidized primitive material and intensely reduced metal, rich in silicon and silicides, are likely.

(b) The variation in temperature between the surface and centre of the molten earth will be much greater than in the meteoritic body, resulting in correspondingly larger displacements of the equilibria concerned.

(c) The high pressure in the interior of the earth will strongly displace chemical equilibria between silicates and metal initially established at lower pressures. This applies particularly to partition of Ni, Si and Fe between metal and silicate (Ringwood, 1959).

(d) The size of the earth is much greater than that of the meteoritic parent planet. In general, it may be expected that when phase separation of the type discussed occurs in a system in which wide variation of compositional, temperature and pressure distribution exists, the larger the system, the more difficult it will be to attain final equilibrium.

The net result, as previously discussed, is that after segregation, followed by independent homogenization of core and mantle, the earth's core will probably contain large quantities of nickel (7 per cent) and silicon (20 per cent) whereas the mantle will still contain some oxidized iron—perhaps 5 per cent. At the core–mantle boundary (C.M.B.) the following reactions will occur

$$Ni + FeO \rightarrow Fe + NiO \qquad \text{(Ringwood, 1959)}$$

$$Si + 2FeO \rightarrow 2Fe + SiO_2$$

Silicon and nickel will diffuse from the core into the mantle and will precipitate metallic iron from the silicates in the region immediately above the core. A consequence of the previous discussion, therefore, is that the mantle should contain a layer overlying the core, which contains appreciable amounts of metallic iron.

It should be emphasized that the previous conclusions concerning non-equilibrium between core and mantle are general, and do not depend strictly upon particular models advanced by the author. They are plausible for a variety of possible models of core segregation.

6. Constitution of the Mantle near the Core–Mantle Boundary

The velocity–depth curves of Jeffreys (1939) and Gutenberg (1958) both display a marked change of slope in the bottom 200 km of the mantle. Gutenberg (1958, 1960) has discussed further seismic evidence relating to this region. The amplitude data and the straight travel–time curves indicate that P- and S-wave velocities are either constant or are decreasing slightly, in contrast to the remainder of the lower mantle, where velocities increase steadily with depth. Lehman (1953) suggests that the occurence of small early P-waves in the shadow zone beyond 102° previously thought to be a diffraction effect, may be caused by a low velocity zone immediately above the core.

In the previous section it was suggested that the core and mantle are out of chemical equilibrium, in consequence of which, metallic iron is being precipitated in the Contact Zone of the mantle, immediately above the core. This would modify the seismic velocities in the right direction. If the contact zone contained about 5 or 10 per cent of metallic iron intermingled with the silicates, the observed flattening, or decrease in seismic velocities would be accounted for. Gutenberg (1958) believes that Poisson's ratio increases with depth in the contact zone. If confirmed, this would provide most significant evidence, since an increase of Poisson's ratio corresponds to a decrease in rigidity compared to compressibility. This could be caused by the presence of some liquid iron trapped in the silicates.

If the above explanation is correct, the contact zone must be mechanically unstable, since liquid iron will tend to migrate downwards through the silicates, and enter the core (Urey, 1952). It is possible that this instability may cause minor localized convective overturns in different regions. The process of sinking and settling out of iron may well get out of phase, so that at any one time, regional differences in iron content may exist. In this respect, it is interesting that Lehman (1958) has suggested from seismic data that "Variations in depth of the core boundary and of the constitution of the bordering regions of the mantle seem to be indicated".

7. Electrochemical Effects at the Core–Mantle Boundary (C.M.B.)

Non-equilibrium between core and mantle, due to the tendency of nickel and silicon to migrate from the core into the mantle and precipitate metallic iron, will cause a potential of the order of 1 V to be established across the C.M.B. (Ringwood, 1959). Whether this will give rise to electric currents flowing between core and mantle, depends upon the mechanism by which equilibrium is reached. Nickel and silicon atoms will become ionized at the C.M.B., and will diffuse through the contact zone accompanied by the equivalent number of electrons, until a region is reached where Fe^{2+} ions are present in the silicates. The Fe^{2+} ions will then be replaced by Ni^{2+} and Si^{4+}, whilst the accompanying electrons reduce Fe^{2+} to metallic iron. Net reactions are

$$Si^0 \rightarrow Si^{4+} + 4e$$
$$Ni^0 \rightarrow Ni^{2+} + 2e$$
$$Fe^{2+} + 2e \rightarrow Fe^0$$

If the contact zone is perfectly homogeneous in electrical properties, the ions and electrons will move along the same paths, no charge separation will occur, and hence equilibrium will be approached without the generation of electric currents. It does not appear likely, however, that the ionic and electronic transport properties of the contact zone will be uniform. Three factors contribute to differences in the transport mechanisms of ions and electrons, and may cause the generation of electric currents between core and mantle.

(1) The contact zone will consist of a mixture of silicates and metallic iron. Electrons will preferentially flow through the metallic iron conductors whilst Ni^{2+} and Si^{4+} ions will diffuse through silicates.

(2) The silicates in the contact zone possess high electronic conductivities (Runcorn, 1955). The ionic and electronic conduction mechanisms may be affected considerably, and differentially by relatively small local variations in chemical composition, leading to charge separation and electric currents.

(3) The reaction between nickel, silicon and oxidized iron in the contact zone liberates chemical heat. Ionic and electronic conduction mechanisms vary exponentially with temperature, and possess different activation energies and constants. It is possible that the localized chemical heating may cause inhomogeneity in transport properties, leading to electric currents. Temperature perturbations, caused by small convective overturns and settling out of iron, may also contribute.

These considerations suggest that the contact zone may be the site of a fundamental mechanical, thermal and electrical instability, and that localized, intermittent electric currents may flow across the C.M.B. under a potential of about 1 V. There is a possibility that these currents may play a significant role in the generation of the earth's magnetic field. The widely accepted "dynamo theory" postulates that convective motions in the earth's core greatly magnify and sustain a small initial magnetic field. There have been difficulties associated with explaining the origin of the small initial field. If, however, this initial field is created by local currents of electrolytic origin flowing across the C.M.B., this difficulty would be removed.

These speculations may be followed further. Is it possible that a relationship exists between the locations of these small "starter currents" at the C.M.B., and the

final configuration of the earth's magnetic field? Convection currents in the earth's core would then function primarily as an amplification mechanism for the small, initial currents and fields, rather than as a self-sustaining generator. Temperature perturbations in the contact zone, as previously discussed, might also upset the regularity and symmetry of the convection currents in the core. These possibilities might lead one to question the view that the earth's magnetic field has always been that of a dipole oriented parallel to the axis of rotation. Perhaps this configuration has alternated in the past with other non-dipole, non-symmetrical configurations, controlled by thermal and electrical perturbations in the contact region. Finally, the earth is known to experience slight irregular changes in the rate of rotation, which may be correlated with changes in the rate of westward drift of the non-dipole field. Rochester (1960) suggests that these changes may be caused by variation in the strength of the electromagnetic coupling between core and mantle. It is conceivable that the tightness of this coupling may be differentially affected by the varying amounts of iron in the contact zone and by local currents flowing in this region. If so, this might lead to lack of symmetry in the coupling strength distribution, and perhaps to differential displacements of the mantle relative to the core.

Acknowledgements—The author is indebted to Prof. J. C. Jaeger and Mr. E. Irving of the Australian National University for their helpful comments on the manuscript, and to Mr. J. Easton, also of the A.N.U., for carrying out the chemical analyses. The author is also greatly indebted to the following individuals and institutions for donations of meteorite specimens used in this study. Mr. R. O. Chalmers, Australian Museum; Dr, H. B. Wiik, Geological Survey of Finland; Dr. K. Fredriksson, Geological Survey of Sweden; Dr. K. R. Dawson, Geological Survey of Canada; Dr. E. Jeremine, Museum d'Histoire Naturelle, Paris; The Director, South African Museum and Dr. M. Hey, British Museum.

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Recherchés physico-chimiques des éléments-traces dans les sols tropicaux—I

I. Etude de quelques sols du Dahomey

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(*Received* 4 *February* 1961)

Abstract—Within the framework of the researches by l'O.R.S.T.O.M. on the composition of tropical soils, a general study was undertaken by l'Institut d'Enseignement et de Recherches Tropicales at Bondy on the distribution of trace-elements in these soils. The purpose of this study is to present evidence of the principal factors connected with these trace-elements.

Resumé—Dans le cadre des recherchés effectuées par l'Office de la Recherche Scientifique et Technique Outre-Mer, sur la connaissance des sols tropicaux, une étude générale a été entreprise à l'Institut d'Enseignement et de Recherches Tropicales à Bondy, sur la répartition des éléments traces et des oligo-éléments dans les sols tropicaux; cette étude a pour but de mettre en évidence les principaux facteurs liés à la présence des éléments traces dans les sols.

Les travaux rapportés ci-dessous concernent quelques sols typiques de la République du Dahomey.‡ Ont été retenus comme sols caractéristiques de cette région: trois sols faiblement ferrallitiques, un sol ferrugineux tropical et un sol noir tropical. La définition de ces sols est conforme à la classification des sols d'Aubert et Duchaufour (1956).

Les prélèvements effectués à différentes profondeurs permettent de suivre l'évolution des éléments traces dans le profil, dans la mesure du possible, depuis la roche mère jusqu'à l'horizon de surface.

Methodes D'Analyses

Chaque échantillon a été soumis à une analyse totale aussi complète que possible, portant sur les constituants de base et les *éléments traces*. Les principaux facteurs paraissant jouer un rôle sur l'évolution des éléments traces sont: pH, matière organique totale, argile, silice, hydroxydes de fer et d'alumine.

Les méthodes chimiques mises en oeuvre sont les suivantes (Ollat et Pelloux, 1957), pH: méthode électrométrique sur une suspension sol/eau égale à 1/2,5, Matière organique totale: dosage du carbone par oxydation au bichromate, Argile: analyse mécanique classique, avec dispersion au pyrophosphate de sodium, Silice, fer, alumine: analyse par attaque aux trois acides, méthode classique.

Les éléments traces recherchés sont: argent, béryllium, bore, chrome, cobalt, cuivre, étain, gallium, germanium, manganèse, molybdène, nickel, plomb, vanadium, zinc.

A l'exception du zinc, déterminé par polarographie, tous les éléments sont

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‡ Les échantillons étudiés ont été prélevés par Fauck (1961), pédologue représentant l'O.R.S.T.O.M., chargé d'une mission d'étude dans ce pays.

recherchés et déterminés par spectrographie d'émission dans l'arc, selon une technique semi-quantitative de comparaison des caractéristiques de raies (Pinta, 1961).

Un échantillon moyen est calciné à 600°C, le résidu, homogénéisé et broyé.

Un premier examen spectrographique est effectué dans les conditions suivantes:

(1) Mélange spectrographié: 25 mg de produit et 25 mg de poudre de graphite.

(2) Électrodes: graphite "Carbone Lorraine" qualité 207; (a) anode, baguette de graphite, de diamètre 5 mm, avec cratère de 3 mm de diamètre et 4 mm de profondeur; (b) cathode, baguette de graphite de 6 mm de diamètre; distance entre les électrodes, 7 mm.

(3) Arc: arc en courant continu 8 A, 60 V en charge, l'échantillon est placé dans l'anode.

(4) Projection de la source sur le collimateur du spectrographe avec emploi d'un secteur à échelons dans le trajet du faisceau.

(5) Spectrographe: appareil Littrow à prisme de quartz (Hilger).

(6) Largeur de fente: 7 μ.

(7) Plaque photographique: Guilleminot, UV rapide ou Ilford-chromatic.

(8) Temps de pose: 1 min 30 sec.

(9) Étalonnage: deux ou trois échantillons synthétiques à teneurs croissantes en éléments traces sont spectrographiés dans les mêmes conditions sur chaque plaque.

Chaque échantillon est analysé deux fois. Les raies sont repérées au comparateur et mesurées au densitomètre. Pour une même plaque, la caractéristique de chaque raie, définie par la densité optique en fonction de l'exposition, est tracée sur un graphique. L'étalonnage est constitué par la courbe suivante:

(1) Ordonnées: position relative des caractéristiques des raies des produits synthétiques d'étalonnage.

(2) Abcisses: concentration ou *log. conc.* des étalons. Les raies utilisées sont (en Ångstroms):

Ag	3280,7	Ge	2651,2
Be	3130,4	Mn	4034,5
Bi	3067,7	Mo	3170,3
Cr	4254,3	Ni	3414,8
Co	3453,5	Pb	2833,1
Cu	3247,5	Sn	2840,0
Ga	2943,6	V	4379,2

Les sensibilités des dosages exprimées par les plus petites concentrations d'éléments en p.p.m. de produit spectrographié sont:

Ag	1	Ge	30
Be	10	Mn	10
Bi	30	Mo	10
Cr	3	Ni	10
Co	3	Pb	10
Cu	1	Sn	10
Ga	10	V	10

Dans les conditions précédentes, ces valeurs sont parfois insuffisantes, pour déceler dans les sols, en particulier, Be, Bi, Co, Ga, Ge, Mo, Pb.

Un second examen spectrographique est effectué de manière à détecter les concentrations 5 à 10 fois plus faibles. Les conditions sont les suivantes.

(1) Électrodes, comme précédemment.

(2) Distance entre électrodes, 2 mm.

(3) Arc, comme précédemment.

(4) Projection de la source sur la fente du spectrographe: projection directe à l'aide d'une lentille.

(5) Temps de pose, 1 min.

(6) Autres conditions, comme précédemment.

La sensibilité obtenue permet de détecter: Mo, 1 p.p.m. Be, Co, Ga, Ge, Sn, Pb, 3 p.p.m. Bi, 10 p.p.m.

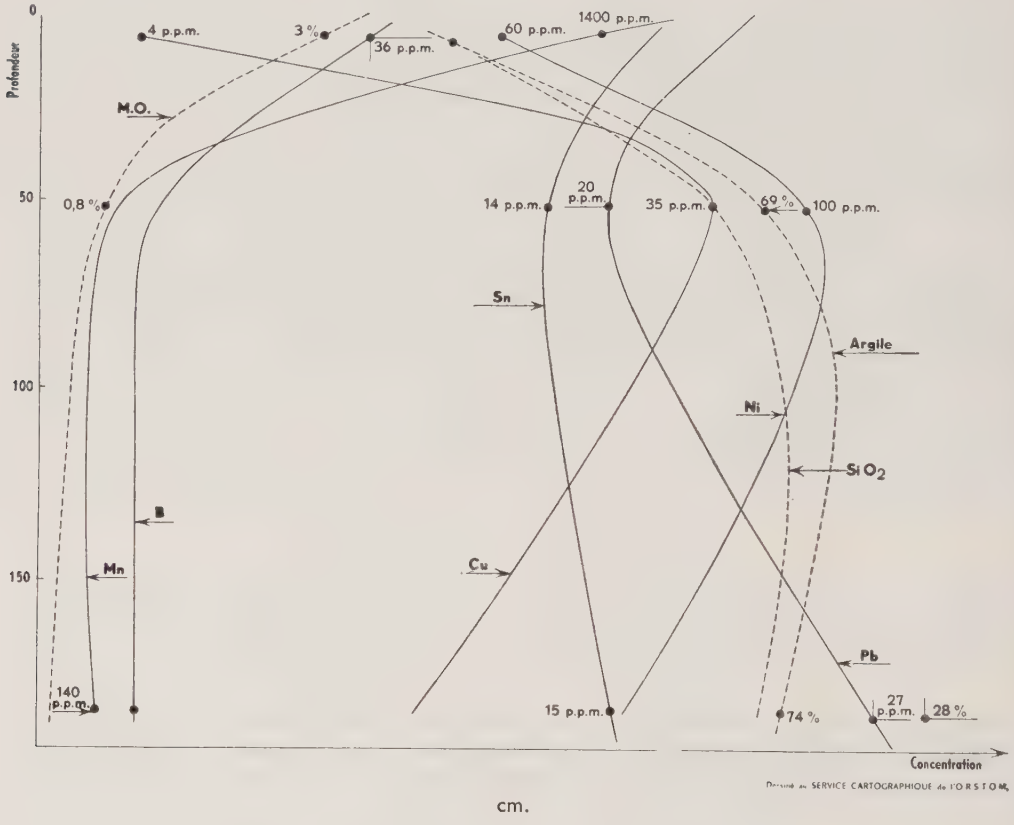

Fig. 1. Sol ferrallitique beige argileux, profil G–13.

La recherche du bore est effectuée d'autre part en utilisant des électrodes en graphite exempt de bore, et en photographiant le spectre dans la région 2500 Å. La raie mesurée du bore est à 2496 Å.

Les examens spectrographiques sont semi-quantitatifs: l'erreur évaluée par une étude statistique préalable est de l'ordre de 20 à 25% environ. La lecture des résultats donnée plus loin montre que cette précision est suffisante dans une telle étude.

Le zinc est déterminé après extraction à la dithizone à pH 8,3, par polarographie

dans un électrolyte de sulfocyanure de potassium-acétate d'ammonium de pH 4,6 (Pinta, 1961).

Etude de Quelques Sols du Dahomey

Sol faiblement ferrallitique beige clair argileux (*G*3–1)

Les résultats d'analyse chimique sont donnés Tableau 1. C'est un sol avec horizon de surface organique; il contient de fortes proportions d'argile (70%) qui augmentent avec la profondeur. Le pH varie de 6,2 en surface à 4,7 à 180 cm. Les éléments traces sont en concentrations relativement fortes; en particulier le manganèse s'accumule de façon notable en surface: la teneur de 1400 p.p.m. associée à un pH acide peut laisser craindre une toxicité sur certaines plantes.

Quelques éléments sont en quantité très faible: Mo, Ge, Be, Bi, Ag. On peut, au point de vue agronomique, soupçonner une carence en molybdène (Mo < 1 p.p.m.).

La répartition des éléments dans le profil du sol est tracée graphiquement Fig. 1: en ordonnées, sont portées les profondeurs des prélèvements, en abcisses, les variations de concentration de chaque élément et constituant du sol: les courbes en trait pointillé, correspondent à la matière organique, à l'argile et la silice (valeurs relatives exprimées en %); les courbes en trait plein traduisent la variation de concentrations des quelques éléments traces: Mn, B, Sn, Pb, Ni.

On constate, dans l'horizon de surface, une accumulation de certains éléments: Mn, B, Sn, Pb, Co. Cette évolution dans le même sens que la matière organique est caractéristique, elle a été signalée antérieurement par Aubert (1956).

En revanche, une zone d'accumulation est située entre 40 et 100 cm pour Cu, Ni, Cr, et au-dessous de 100 cm pour Ga et V. Ces variations peuvent être mises en parallèle avec l'évolution de la teneur en argile.

Sol faiblement ferrallitique beige à hydromorphie temporaire (*E*–3)

Les résultats d'analyse sont notés Tableau 2. Le sol est pauvre en matière organique, à teneur moyenne en argile, et de pH 5: les concentrations d'éléments traces sont plus faibles que dans le sol précédent: il est particulièrement pauvre en Mo, Ag, Ge, Bi, Be. L'évolution de la matière organique, de l'argile et des hydroxydes, et des éléments traces est représenté Fig. 2.

On constate dans l'horizon organique une faible accumulation de Mnet Ni; mais dans l'ensemble il y a augmentation de concentration des éléments avec la profondeur: Pb, Mn, Ni, Co, et également V, Cr, Ga, Sn, Cu, Zn; ces variations sont souvent très fortes: le plomb varie de 30 p.p.m. (à 150 cm) à 3 p.p.m. en surface, le vanadium, de 150 à 10 p.p.m. Cette évolution des éléments traces dans le profil doit être mise en corrélation avec l'argile et les hydroxydes qui varient également dans le même sens.

Sol ferrugineux tropical (*HA*–21)

Les résultats analytiques sont notés Tableau 3. C'est un sol relativement pauvre contenant d'assez fortes quantités de quartz (40 à 60%) dont une partie se retrouve avec l'argile. Les silicates de fer et d'aluminium sont faibles. Le pH varie de 6,1 en surface à 4,6 à 100 cm. Les éléments traces sont en concentrations faibles en surface, ils augmentent avec la profondeur. Le molybdène est de l'ordre de 1 p.p.m., le

Tableau 1. Sol feiblement ferrallitique, beige clair, argileux (G–13). Analyse chimique

Profondeur (cm)	M.O. (%)	Argile (%)	Fe_2O_3 (%)	Al_2O_3 (%)	SiO_2 (%)	Mn (p.p.m.)	Pb (p.p.m.)	Ga (p.p.m.)	Sn (p.p.m.)	V (p.p.m.)	Cu (p.p.m.)	Ni (p.p.m.)	Co (p.p.m.)	Cr (p.p.m.)	Zn (p.p.m.)
0–10	3	32	2,4	14	15	1400	23	15	16	60	4	60	23	90	116
40–60	0,8	69	2,6	25	22	200	20	28	14	85	35	100	18	160	148
180–190	0,3	74	4,1	28	24	140	27	32	15	125	20	80	11	130	85

pH 6,2 à 4,7.
Quartz: dans l'argile faible 1%.
Mo, <1 p.p.m., Ge, <3 p.p.m., Be, <3 p.p.m., Bi, <10 p.p.m.
Ag, traces on surface, 5 p.p.m.
M.O. matière organique.

Tableau 2. Sol faiblement ferrallitique, beige, à hydromorphie temporaire (E- 3). Analyse chimique

Profondeur (cm)	M.O. (%)	Argile (%)	Fe_2O_3 (%)	Al_2O_3 (%)	SiO_2 (%)	Mn (p.p.m.)	Pb (p.p.m.)	Ga (p.p.m.)	Sn (p.p.m.)	V (p.p.m.)	Cu (p.p.m.)	Ni (p.p.m.)	Co (p.p.m.)	Cr (p.p.m.)	Zn (p.p.m.)
0–15	0,8	5				200	3	<3	<3	10		45	<3	35	65
15–35	0,55	18	1	5	7	120	5	<3	<3	30	<1	40	11	50	130
95–105	0,35	45	4	18	21	360	17	20	4	90	1	73	22	140	280
140–160		47	6	20	24	650	30	25	5	150	4	100	30	210	

pH 5.
Mo, <1 p.p.m. en surface, 1 p.p.m. en profondeur.
Ag, <1 p.p.m., Ge, <3 p.p.m., Bi, <10 p.p.m., Be, <3 p.p.m.

Tableau 3. Sol ferrugineux tropical (HA–21). Analyse chimique

Profondeur (cm)	M.O. (%)	Argile (%)	Fe_2O_3 (%)	Al_2O_3 (%)	SiO_2 (%)	Mn (p.p.m.)	Pb (p.p.m.)	Ga (p.p.m.)	Sn (p.p.m.)	V (p.p.m.)	Cu (p.p.m.)	Ni (p.p.m.)	Co (p.p.m.)	Cr (p.p.m.)	Zn (p.p.m.)
0–20	1	8	1,5	2,5	4	155	9	<3	3	25	<1	16	2	60	65
40–60	0,6	30	4,1	8	11	170	11	10	9	66	<1	40	12	100	60
80–100	0,6	40	0,8	0,5	16	190	14	14	9	86	<1	47	16	108	50

pH, 6,1–4,6.
Forte quantité de quartz dans l'argile, 88 à 58%.
Mo, 1 p.p.m. à 50 et 100 cm. Be, 3 p.p.m. à 100 cm.
Ge, <3 p.p.m., Bi, <10 p.p.m., Ag, <1 p.p.m.

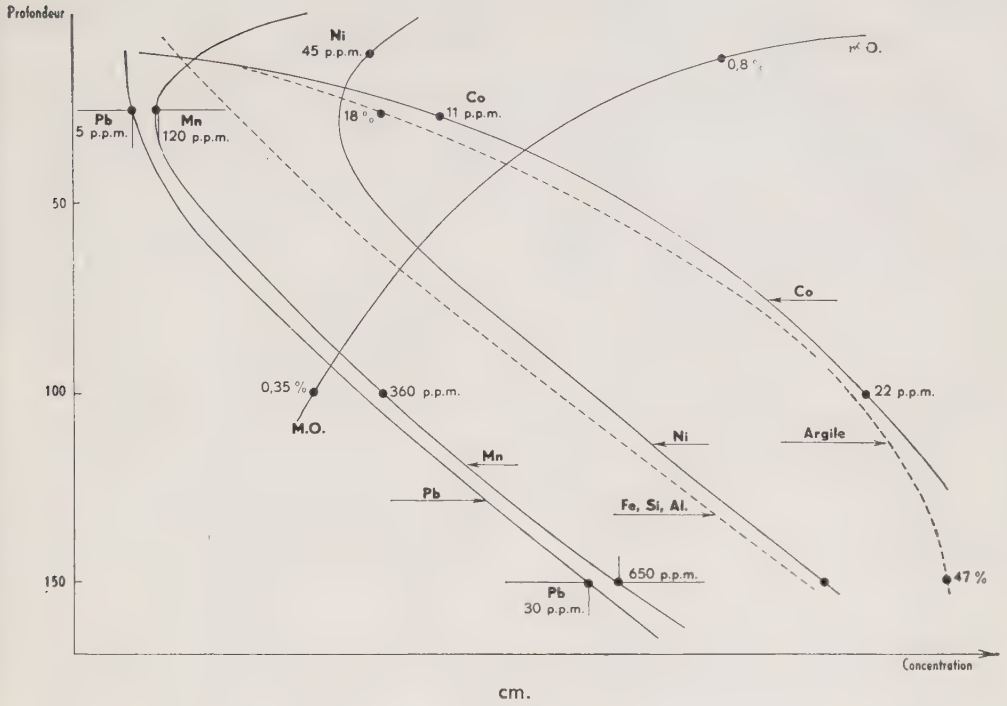

Fig. 2. Sol faiblement ferrallitique beige à hydromorphie temporaire, profil E–3.

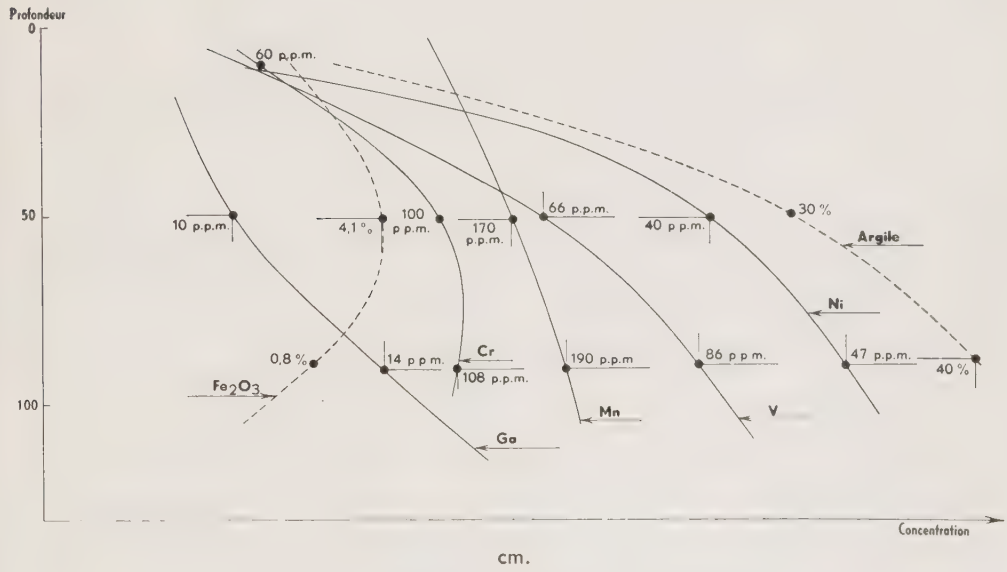

Fig. 3. Sol ferrugineux tropical, profil HA–21.

béryllium 3 p.p.m. Les courbes représentatives sont tracées Fig. 3. On remarque la forme caractéristique de la courbe Fe_2O_3 (Al_2O_3 est semblable): on retrouve cette forme de courbe avec Cr, ainsi qu'avec V et Ni, mais plus atténuée.

Sol type "terre de barre" faiblement ferrallitique sur sédiments tertiaires (*N*–13)

Les résultats analytiques sont notés Tableau 4. C'est un sol assez bien pourvu en matière organique, riche en argile accompagnée de quartz. Le pH varie avec la

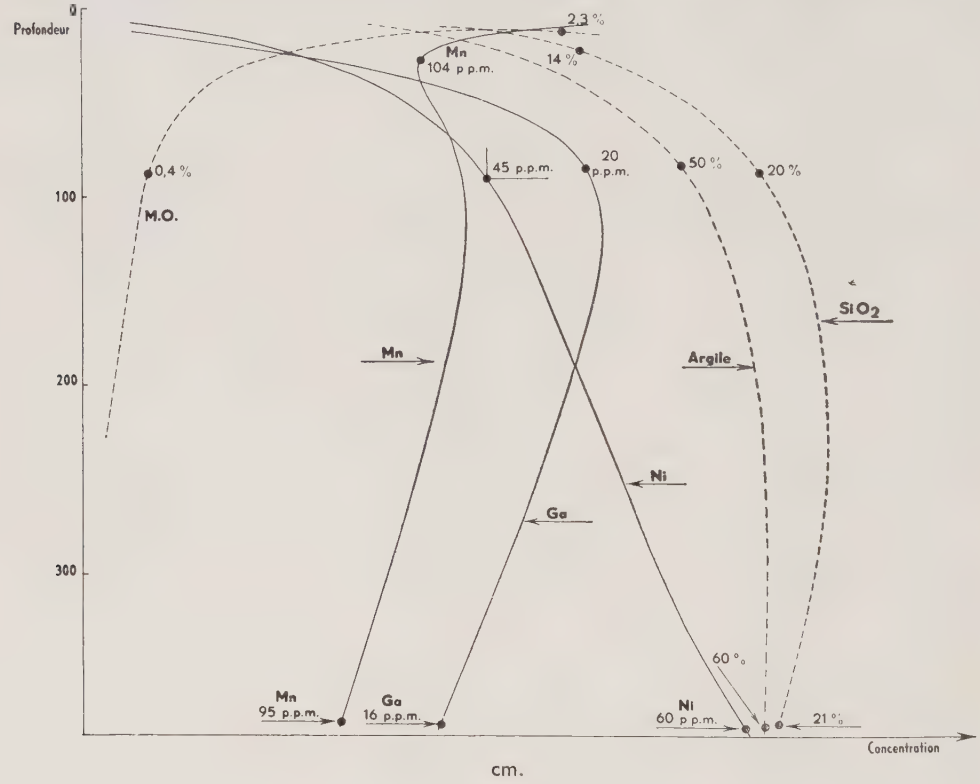

Fig. 4. Sol type "terre de barre" faiblement ferrallitique sur sédiments tertiaires, profil N–13.

profondeur de 4,7 à 4,4. Le sol est riche en éléments traces dans l'ensemble. Le cuivre est toutefois en quantités faibles, inférieures à 1 p.p.m. ainsi que le molybdène, 1 p.p.m. Les courbes de répartition des éléments sont tracées Fig. 4. On retrouve encore une accumulation de manganèse et de bore dans l'horizon organique mais, pour la plupart des éléments traces, les plus fortes concentrations sont situées entre 100 et 200 cm: Pb, Ga, V, Cr, et, au delà de 200 cm: Ni, Zn. On doit envisager là encore une corrélation avec les teneurs en argile et en silicates.

Sol noir tropical à hydromorphie temporaire de surface (*HA*–31)

Les résultats analytiques sont indiqués Tableau 5. Ce sol de pH 6 à 7,4 est particulièrement riche en matière organique, en argile, en éléments traces et oligo-éléments à l'exception toutefois du cuivre. La répartition des principaux constituants du sol et des éléments traces est représentée par les courbes de la Fig. 5.

Tableau 4. Sol type "terre de barre" faiblement ferrallitique sur sédiments tertiaires (N–13). Analyse chimique

Profondeur (cm)	M.O. (%)	Argile (%)	Fe_2O_3 (%)	Al_2O_3 (%)	SiO_2 (%)	Mn (p.p.m.)	Pb (p.p.m.)	Ga (p.p.m.)	Sn (p.p.m.)	V (p.p.m.)	Cu (p.p.m.)	Ni (p.p.m.)	Co (p.p.m.)	Cr (p.p.m.)	Zn (p.p.m.)
0–15	2,3	19				130	15	9	3	46	<1	26	3	35	40
20–30	0,6	35	4,6	10	14,5	104	20	13	3	95	<1	36	6	95	70
80–90	0,4	50	5	11	20	110	22	20	3	120	<1	45	6	120	80
375–385	0,2	60	5,8	18	21	95	20	16	3	108	<1	60	<3	100	100

pH, 4,7–4,4.
Quartz, forte quantité dans l'argile, 63 à 45%.
Mo, 1 p.p.m. à 80 et 380 cm.
Be, 7 à 10 p.p.m. à 80 et 380 cm.

Tableau 5. Sol noir tropical à hydromorphie temporaire de surface (HA–31). Analyse chimique

Profondeur (cm)	M.O.	Argile (%)	Fe_2O_3 (%)	Al_2O_3 (%)	SiO_2 (%)	Mn (p.p.m.)	Pb (p.p.m.)	Ga (p.p.m.)	Sn (p.p.m.)	V (p.p.m.)	Cu (p.p.m.)	Ni (p.p.m.)	Co (p.p.m.)	Cr (p.p.m.)	Zn (p.p.m.)
0–20	5	43	7	6	19	2000	14	10	27	85	<1	33	16	103	80
60–80	0,7	62	6,3	12	30	1%	22	14	14	125	<1	43	60	130	80
150	0,3		8,1	15	43	1%	13	14	3	150	<1	56	50	150	102
200	0,3		6,3	16	46	250	9	17	3	160	<1	35	10	160	114

pH, 6 à 7,4.
Mo, 3 p.p.m. en surface, 8 à 10 p.p.m. en profondeur
Ge, <3 p.p.m., Bi, <10 p.p.m.

L'étain est le seul élément paraissant s'accumuler dans l'horizon organique. Des zones d'accumulation sont caractéristiques vers 100 à 200 cm pour B, Co, Ni, Pb, et à des profondeurs plus fortes pour Ga, V, Cr. Il semble, là encore, que l'argile soit responsable de cette répartition caractéristique des éléments traces dans le profil.

La concentration de manganèse est très forte: la zone d'accumulation entre 80 et 150 cm contient plus de 1% de manganèse. Cette teneur n'est trouvée que très rarement dans les sols.

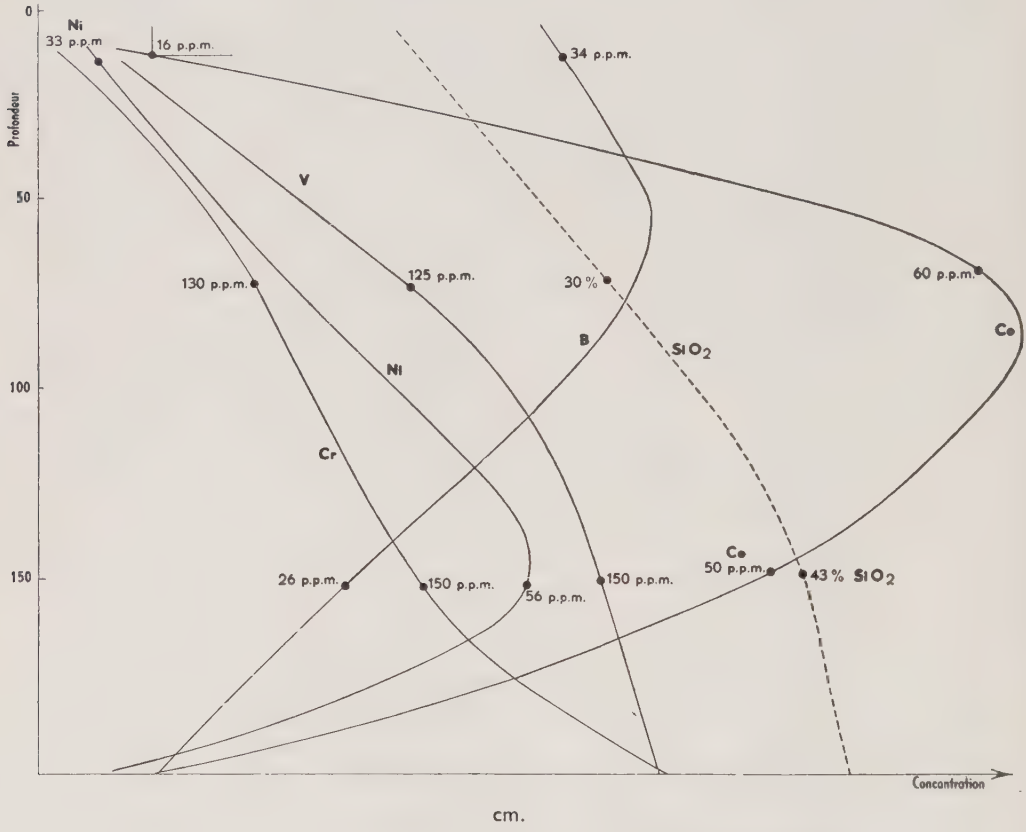

Fig. 5. Sol noir tropical à hydromorphie temporaire de surface, profil HA–31.

Observations Générales et Conclusions

L'examen de ces résultats appelle quelques remarques.

(1) Si l'on compare les valeurs d'éléments traces trouvées dans ces sols aux teneurs moyennes des sols normaux, on remarque que les éléments B, Mn, Pb, Ga, Sn, V, Ni, Co, Cr, Zn, sont à des concentrations normales dans les sols étudiés, à l'exception de Mn que l'on trouve dans le sol noir tropical (HA–31) à une concentration anormalement forte.

D'autre part, les éléments Cu et Mo sont souvent trouvés dans les sols dahoméens, à des concentrations inférieures à leurs concentrations moyennes dans les sols normaux (Cu 2–100 p.p.m. et Mo 1–4 p.p.m.).

En conséquence, on peut, dans l'interprétation agronomique de ces résultats, soupçonner des carences en cuivre et molybdène.

(2) L'examen général des résultats montre que dans toute prospection géochimique, pédologique, agronomique, le seul examen de l'horizon de surface ou d'un horizon peu profond ne donne pas de renseignements suffisants sur la teneur du sol en éléments traces.

(3) On trouve fréquemment dans l'horizon organique des accumulations de bore et manganèse, et, plus rarement, de Pb, Ni, Sn.

(4) D'une façon générale, la concentration des éléments traces varie, à l'intérieur du profil, dans le même sens que la concentration d'argile: on constate, en particulier, des accumulations d'éléments dans l'horizon argileux.

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Geochemical analysis of Italian oils and asphalts

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(*Received in revised form*, 1 *December* 1960)

Abstract—Seventy oil and asphalt shows from continental Italy and Sicily were sampled and studied. They were subdivided into five geographical regions, which broadly correspond to geologic provinces.

The geochemical method employed involves the fractionation of the oils and asphalts into their different constituents (oily components, resins, asphaltenes and carbenes), as well as the analysis of oily components (elementary analysis, molecular weight and infra-red spectra determination). Spectrographic determination of trace metals was also made in most of the samples. Two methods were employed for the fractionation: solvent extraction and chromatography.

A geochemical correlation among the different oils and asphalts within each region was made. The structural differences found among the various oils of each basin were attributed essentially to environmental factors. Remarkable analogies were noticed among the oils from different basins: this is in agreement with the findings on the simple constitution of crude oils and with the ideas on the genesis of petroleum by the selective preservation of naturally occurring hydrocarbons and by minor modifications of organic matter.

Introduction

Among European countries, Italy presents perhaps the highest abundance of hydrocarbon shows. Petroleum shows, which are particularly abundant in the Apennine system and in Sicily, are distributed throughout a wide area of sedimentary rocks and are found in formations ranging in age from Triassic to Pleistocene. Among surface shows, particularly important are the asphalt accumulations of Abruzzi and Sicily, whose known reserves are of the order of several hundred million tons. Bituminous seepages are found in Tosco-Emilian Apennine and in Central-Southern Apennine: they are of minor importance from the quantitative point of view, but there is no doubt of their petroliferous significance. In Sicily, where asphalt shows are also very abundant, oil seepages have been known for several centuries.

In spite of the widespread distribution of petroleum shows in Italy, the reserves of oil which have been ascertained in commercial reservoirs are relatively meagre.

A systematic study of Italian oil shows was carried out by Zuber (1938, 1939) Zuber considered the various hydrocarbon shows with particular reference to the geological profile and based his correlation on morphological and stratigraphic characteristics.

Other attempts at general correlation of Italian shows were made during the same period (Gortani and Migliorini, 1937), while certain authors have attempted correlations on a more strictly regional basis (Camerana and Galdi, 1926; Greig, 1937).

A physicochemical study of Italian oils was more recently made by Facca *et al.* (1951) who made a structural analysis of several oils, and attempted a correlation between the structure of such crude oils and the ages and depths of reservoir rocks.

With the present work a geochemical correlation of Italian oil and asphalt shows is presented. This correlation is based upon a study of the structural composition of oils and the determination of their degree of evolutive maturity.

Petroleum geochemistry is a relatively young science, which, however, has undergone a tremendous development in recent years, yielding important contributions both from the point of view of oil exploration and of the more speculative research on the formation, migration and accumulation of hydrocarbons. A basic work of this nature has been performed in Germany by Krejci-Graf (1955), and in France by Louis (1951, 1954) and his co-workers of the Institut Français du Pétrole. These latter investigators have developed a method of analysis and interpretation which led them to a geochemical classification of oils and asphalts. Their work, applied to the study of particular petroliferous regions (Bienner *et al.*, 1955; Louis and Bienner, 1953), has shown how the practical usefulness of oil geochemistry is coupled with a high degree of scientific interest.

The chemical aspects of the origin, migration and accumulation of petroleum have been intensively studied in the United States of America, particularly after the stimulating work by Whitmore (1944). The idea that hydrocarbons from animals and vegetation, preserved in the sediments under favourable conditions, give a primary contribution to the formation of petroleum, was supported by the work of Smith (1954), Swain (1954) and of several other investigators. Later work by Stevens *et al.*(1956) and by Erdman *et al.* (1958) has indicated that the preservation of naturally occurring hydrocarbons must be integrated with some different processes in order to account for the formation of petroleum. Decarboxylation of fats, cyclization of unsaturated compounds and disproportionation reactions are among the most important processes that are believed to play a role in the formation of petroleum (Breger, 1959; Meinschein and Kenny, 1957; Meinschein, 1958).

In recent years the migration and accumulation of oil has been a matter of great interest to petroleum geochemists, who have considered new mechanisms which are more consistent with the recent ideas on the origin of oil (Baker, 1956, 1958; Dickey and Kidwell, 1958; Roof and Rutherford, 1958) than with the classical ones. These new mechanisms involve the migration of oil dispersed in the aqueous phase, both as a molecular solution and as a micellar dispersion stabilized by electrochemical and physicochemical forces.

The problems of geochemical alteration of hydrocarbons have been intensively studied in the last few years. The formation of resins, asphaltenes, carbenes as a result of reactions of polymerization, oxidation and dehydrogenation has been shown by the work of French investigators (Bienner *et al.*, (1955).

The classical ideas on the formation of hydrocarbons from complex organic matter and their migration from the source rock to the reservoir rock, mainly as a petroleum phase, have evolved considerably during the past few years. In the interpretation of geochemical work, the assumption of the validity of the classical mechanism would be a serious limitation to the attainment of valid conclusion concerning the genesis and evolution of oils and asphalts.

Geographical Distribution of Shows and Collection of Samples

Seventy different oil or asphalt shows were sampled for examination. Of these, thirty-two were crude oil shows, mostly from oil fields of continental Italy and

Sicily, whereas the remaining thirty-eight were shows consisting of asphalt-bearing rocks, from which the asphalt was separated by extraction.

The volume of each available oil sample was of the order of from 1 to 2 l. Asphalt samples of from 100 to 200 g each were generally sufficient for all the geochemical analyses.

In Fig. 1, the geographical distribution of Italian shows is indicated. Table 1 gives a list of the shows considered in the work, with the corresponding data on lithology, age and depth of the host formations.

In the study of the Italian oil and asphalt shows, the country has been subdivided into five geographical regions, which, in general, correspond to geologic provinces. They are:

(1) Eastern Alps and Adige Valley area: This region belongs to the Eastern folded and overthrusted ridge of the Alps (Dinarides) and is characterized by a thick Mesozoic section strongly affected by compressive tectonics. It is well known through classical geologic works (Dal Piaz, 1945).

(2) Po Valley and Northern Apennine area: This area corresponds to a large structural–sedimentary basin having its Tertiary foreland to the north-north-east and its inner rim to the south-south-west. The broad stratigraphic complexes, in terms of fluid dynamics, are the following (from top downward): (a) shaly–sandy complexes, ranging in age from Oligocene to Pleistocene. A very important characteristic of this sequence is the presence of huge olistostromes* (''argille scagliose'') intercalated between Lower Middle Miocene and Upper Miocene–Pliocene; (b) carbonate section ranging in age from Eocene to Upper Triassic; (c) shaly–gypsiferous section of Triassic age.

(3) Central Apennine area: This area comprehends the Marche-Abruzzi basin and its western rim, rising towards the Tyrrhenian Sea (Lazio Area). The Tertiary foreland of this basin lies in the Adriatic Sea. The stratigraphy is similar to that of area 2) but the carbonate sedimentation has continued up through the Middle Miocene and the shaly–sandy section covers Upper Miocene, Pliocene and Pleistocene. Olistostromes are not present in this basin.

(4) Southern Apennine area: This area is formed by a basin narrower than those of Po Valley and of Marche-Abruzzi, of which it is the southern extension. The main differences with respect to the Central Italy basin are: (a) the presence of thick olistostromes intercalated in the Middle Miocene and Lower Pliocene formations; (b) the great thickness of the carbonate section, which may reach more than 15,000 ft and which is characterized by platform facies instead of the open-sea facies of central and northern Italy.

(5) Sicily: The Sicilian basin is very similar to that of Southern Apennine. Olistostromes are present all over northern and central Sicily and they were inplaced in ages ranging from Middle Miocene to Pleistocene. In central and northern Sicily the carbonate section ends with the Eocene limestones while the sandy–shaly section starts with Oligocene; in the Ragusa Plateau the entire

* Note: The term ''olistostromes'' is used to indicate masses of chaotic ''slump'' material, which are found intercalated with ''normal'' sediments and are classified as particular stratigraphic units. Olistostromes enclose blocks of more or less porous rocks: such exotic blocks are named ''olistoliths'' (Flores, 1959).

Fig. 1. Geographic distribution of studied oil and asphalt shows (see Table 1).

Table 1. List of studied oil and asphalt shows from continental Italy and Sicily

No.	Type of show	Locality	District	Lithology	Host-rock Age	Depth
A. *Eastern Alps Area (Adige Valley)*						
1	asphalt	Tres 1	Trento	limestone	Cretaceous	outcrop
2	asphalt	Tres 2	Trento	limestone	Cretaceous	600 ft
3	asphalt	Cortaccia	Trento	limestone	Triassic	outcrop
4	asphalt	Mollaro 1	Trento	marl	Cretaceous	outcrop
5	asphalt	Mollaro 2	Trento	marly limestone	Cretaceous	outcrop
6	asphalt	Zambana	Trento	dolomite	Triassic	outcrop
7	asphalt	Valle dei Tovi	Trento	limestone	Triassic	outcrop
8	oil	Cavedine	Trento	limestone	Triassic	outcrop
B. *Po-Valley and Northern Apennine Area*						
9	oil	Cortemaggiore	Piacenza	sand	Upp. Miocene	5000 ft
10	oil	Montechino	Piacenza	sandst. (olistostroma)	Upp. Tertiary	1700 ft
11	oil	Salsomaggiore	Parma	sand	Low. Miocene	650 ft
12	oil	Velleia	Parma	sandst. (olistostroma)	Upp. Tertiary	900 ft
13	oil	Vallezza	Parma	sand (olistostroma)	Upp. Tertiary	800 ft
14	oil	Vallezza	Parma	sand (olistostroma)	Upp. Tertiary	3000 ft
15	oil	Vizzola	Parma	sand	Upp. Miocene	2400 ft
16	oil	Salsominore	Parma	sand	Low. Miocene	2000 ft
17	oil	Pavullo	Modena	sandst. (olistostroma)	Upp. Tertiary	1000 ft
18	oil	Pietramala	Firenze	limest. (olistostroma)	Upp. Tertiary	2600 ft
19	oil	Selvapiana	Forli	sandstone	Low. Miocene	700 ft
20	oil	Perticara	Pesaro	gypsif. shale	Upp. Miocene	sulphur mine
C. *Central Apennine Area*						
21	oil	Alanno (C 12)	Pescara	limestone	Mid. Miocene	2300 ft
22	oil	Alanno (C 1)	Pescara	calcarenite	Low. Miocene	2800 ft
23	oil	Alanno (C 20)	Pescara	calcarenite	Low. Miocene	2400 ft
24	oil	Alanno (C 18)	Pescara	calcarenite	Low. Miocene	2400 ft
25	asphalt	Alanno (C 2)	Pescara	marly limestone	Cretaceous	3400 ft
26	asphalt	Scafa	Pescara	calcarenite	Low. Miocene	outcrop
27	asphalt	S. Spirito	Pescara	calcarenite	Eocene	outcrop
28	oil	Tocco Casauria	Pescara	sandstone	Mid. Miocene	600 ft
29	asphalt	S. Potito	L'Aquila	limestone	Cretaceous	outcrop
30	asphalt	Celano	L'Aquila	limestone	Cretaceous	outcrop
31	oil	Casalbordino	Chieti	calcarenite	Cretaceous	10,000 ft
32	asphalt	Petacciato	Campobasso	limestone	Miocene	5000 ft
33	asphalt	Filettino	Frosinone	dolomite	Triassic	outcrop
34	asphalt	Alatri	Frosinone	dolomite	Triassic	outcrop
35	oil	S. Giovanni Incarico	Frosinone	sandstone	Miocene	1500 ft
D. *Southern Apennine Area*						
36	asphalt	Baranello	Campobasso	limest. (olistostroma)	Upp. Tertiary	outcrop
37	asphalt	Mutria	Benevento	sandst. (olistostroma)	Upp. Tertiary	outcrop
38	asphalt	Colle Sannita	Benevento	sandst. (olistostroma)	Upp. Tertiary	outcrop
39	oil	Ginestra degli Schiavoni	Benevento	shale (olistostroma)	Upp. Tertiary	outcrop
40	oil	Pietrelcina	Benevento	shale (olistostroma)	Upp. Tertiary	outcrop
41	asphalt	Lapio	Avellino	sandst. (olistostroma)	Upp. Tertiary	outcrop
42	asphalt	S. Angelo dei lombardi	Avellino	limestone	Cretaceous	outcrop
43	asphalt	Serino	Avellino	limestone	Cretaceous	outcrop
44	asphalt	Solofra	Salerno	limestone	Upp. Triassic	outcrop
45	asphalt	Ospedaletto	Avellino	limestone	Jurassic	outcrop
46	asphalt	Paestum	Salerno	calcarenite	Miocene	outcrop
47	asphalt	Corleto Monforte	Salerno	limestone	Cretaceous	outcrop
48	oil	Tramutola	Potenza	dolom. (olistostroma)	Upp. Tertiary	900 ft
49	asphalt	S. Martino d'Agri	Potenza	calcarenite	Miocene	outcrop
50	asphalt	Latronico	Potenza	limest. (olistostroma)	Upp. Tertiary	outcrop
51	oil	Oriolo	Cosenza	marl (olistostroma)	Upp. Tertiary	outcrop
52	asphalt	Albidona	Cosenza	limest. (olistostroma)	Upp. Tertiary	outcrop

Table 1—(*contd.*)

No.	Type of show	Locality	District	Lithology	Host-rock Age	Depth
E. *Sicily*						
53	asphalt	Marineo	Palermo	dolomite	Triassic	outcrop
54	asphalt	Ponte Bagni	Trapani	marly limestone	Cretaceous	outcrop
55	oil	Petralia	Palermo	sandstone	Mid. Miocene	outcrop
56	oil	Avanella	Palermo	limestone	Eocene	6500 ft
57	aspahlt	S. Giorgio	Palermo	mar. lim. (olistostroma)	Upp. Tertiary	outcrop
58	asphalt	Nicosia	Enna	sandst. (olistostroma)	Upp. Tertiary	outcrop
59	oil	S. Agrippina	Enna	sandst. (olistostroma)	Upp. Tertiary	outcrop
60	oil	Bivona	Agrigento	sandst. (olistostroma)	Upp. Tertiary	outcrop
61	oil	Barrafranca	Caltanissetta	gypsif. shale	Upp. Miocene	sulphur mine
62	asphalt	Gela	Caltanissetta	dolomite	Triassic	10,000 ft
63	asphalt	Vittoria	Ragusa	dolomite	Triassic	7300 ft
64	asphalt	Ragusa	Ragusa	limestone	Oligocene	outcrop
65	oil	Ragusa	Ragusa	dolomite	Triassic	6000 ft
66	asphalt	Castelluccio	Ragusa	calcarenite	Mid. Miocene	outcrop
67	oil	Noto	Siracusa	dolomite	Triassic	8700 ft
68	asphalt	Fortugno	Ragusa	limestone	Jurassic	3600 ft
69	asphalt	Streppenosa	Ragusa	calcarenite	Mid Miocene	outcrop
70	oil	Streppenosa	Ragusa	basalt	Jurassic	3700 ft

Tertiary section is formed by limestones and calcarenites. In the central part of the basin the top of the carbonate section, which outcrops on both sides of the basin, lies at depths of the order of 20,000 ft.

Analytical Procedures

The geochemical work proceeded along the following lines:

(a) Determination of the degree of evolutional maturity of shows.
(b) Structural analysis of oily components.
(c) Determination of the physicochemical properties of oils or asphalts, useful for correlation purposes.

Fractionation methods

Oils and asphalts were fractionated in order to obtain the pure oily components after separation of the different products of alteration (resins, asphaltenes, carbenes). The geochemical fractionation process employed is that developed by Louis and co-workers (Bienner *et al.*, 1955; Louis, 1951), which is schematically represented in Fig. 2(a). In the case of asphalt-bearing rocks, a preliminary extraction with boiling chloroform was performed by a 2 l. Kumagawa extractor. When necessary, the extraction of carbenoids from the host rock was performed using boiling α-chloronaphthalene.

In the geochemical analysis of crude oils the most volatile fraction (boiling point $< 300°C$) was eliminated by vacuum distillation prior to the fractionation process, in order to be able to compare the data of the geochemical analyses of the non-volatile fractions of oils with those of the corresponding fractions of asphalts.

Several of the shows studied were submitted to the chromatographic fractionation process developed by Kleinschmidt (1955), which is schematically represented in Fig. 2(b). The oily components are obtained with this method as two

separate fractions, namely white oils and dark oils. The total amount of white and dark oils corresponds, with good precision, to the amount of the oily components obtained with the LOUIS method; however, the white oils are practically free of oxygenated compounds. The resins of the LOUIS method are equivalent to the sum of two fractions obtained with the Kleinschmidt method: the "asphaltic resins" and the "acetone–chloroform desorbed". The advantage of this method

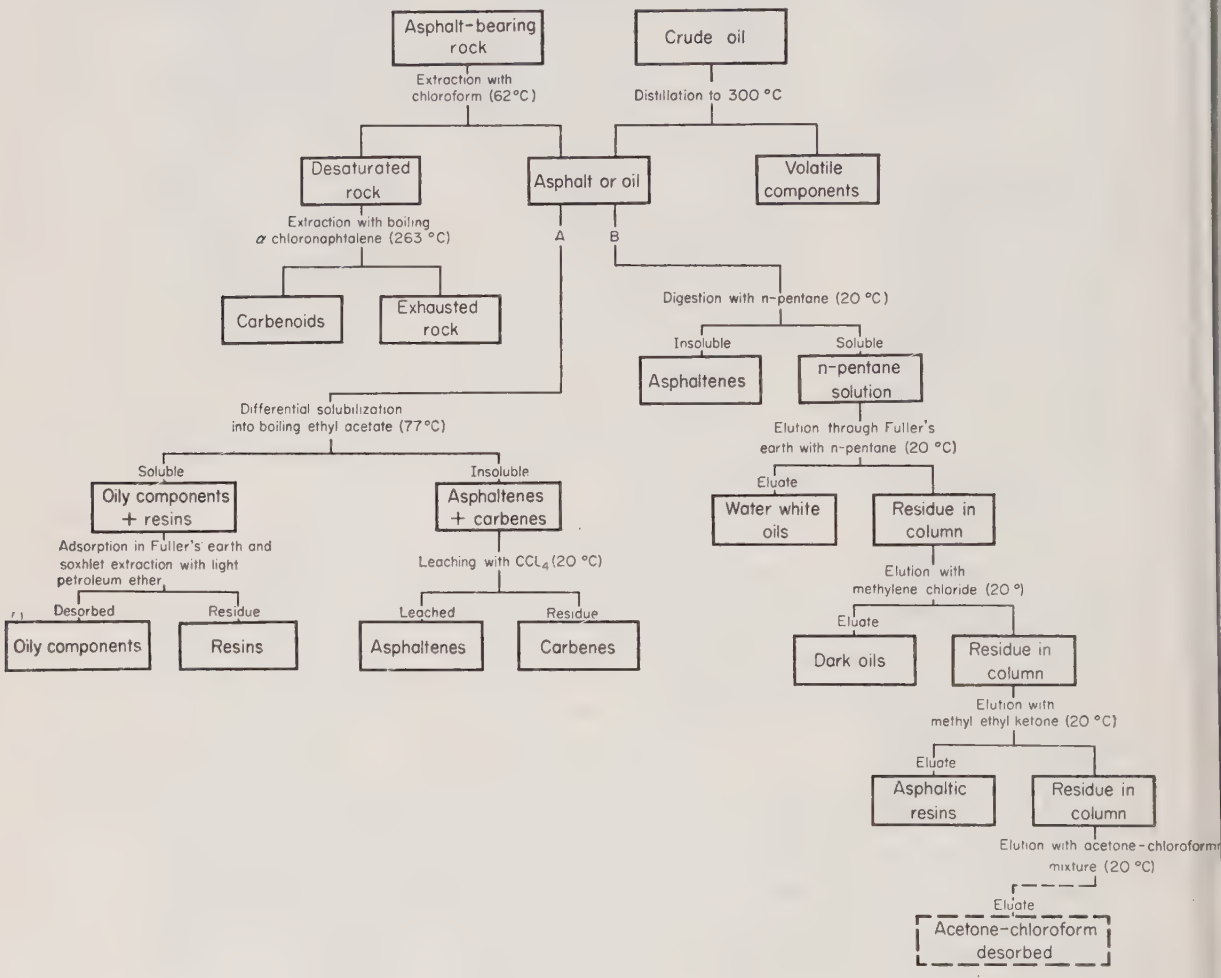

Fig. 2. Scheme of geochemical fractionations of oils and asphalts (KLEINSCHMIDT, 1955; LOUIS, 1951).

of fractionation lies in the fact that a more detailed separation of the different constituents of each show is made possible without a substantial increase in the time of analysis.

Experiments were performed on one of the asphalts studied (show no. 69), with the purpose of establishing the degree of reproducibility of the LOUIS and KLEINSCHMIDT fractionation methods (see Table 2).

Both methods proved to be sufficiently reliable for applied geochemical work.

The concentrations of oily components and resins with the LOUIS method are reproducible within plus or minus 1 per cent. The same degree of reproducibility is attained also on the asphaltene and carbene fractions, if temperature is kept constant during the leaching with CCl_4.

The KLEINSCHMIDT method gives results which are also reproducible with good precision, but here the temperature effect is more remarkable, and it affects all the fractions obtained.

Table 2. Data from analytical fractionation of an asphalt (show no. 69) using the methods of LOUIS and KLEINSCHMIDT (see Fig. 2).
(Fractionations nos. 1–4 were carried on at a temperature of 20°C; fractionations nos. 5–6 at 15°C; fractionations nos. 7–8 at 25°C.)

LOUIS method					KLEINSCHMIDT method					
Fractionation no.	Oily comp. (%)	Resins (%)	Asphaltenes (%)	Carbenes (%)	Fractionation no.	White oils (%)	Dark oils (%)	Asphaltic resins (%)	Acetone-chloroform desorbed (%)	Asphaltenes + + carbenes (%)
1	58·32	24·15	10·36	7·17	1	38·35	20·52	12·15	10·13	18·83
2	59·47	23·96	10·91	5·66	2	39·04	19·17	13·09	8·48	20·22
3	58·63	24·48	11·38	5·51	3	37·91	20·81	13·62	7·99	19·67
4	58·25	25·03	10·01	6·71	4	38·59	19·96	11·20	10·94	19·31
5	58·46	24·21	9·15	8·18	5	35·82	20·14	14·01	7·12	22·91
6	59·35	23·47	8·25	8·93	6	36·81	19·61	13·14	7·29	23·15
7	59·12	23·73	12·13	5·01	7	40·69	19·82	12·31	9·20	17·98
8	57·95	24·54	12·19	5·32	8	39·92	20·21	11·87	10·66	17·34

Analysis of oily components

The oily components obtained with the method described above were carefully studied in order to determine their structure. A semimicro elementary analysis was performed and the average molecular weight was determined by the ebullioscopic method. (VAN NES and VAN WESTEN, 1951.)

Infra-red spectra were run on oily components and on the white and dark oils. These samples were examined, without solvent, with a cell thickness of 0·05 mm. In several shows infra-red spectra were run also on resins and asphaltenes, which were examined as thin films obtained by evaporation from solutions (thickness in the order of 0·005 mm).

Trace-metals determination

Whenever a sufficient amount of oil or asphalt was available, a spectrochemical study was carried out in order to determine the trace-metals concentrations for correlation purposes. A wet-ash spectrographic method of analysis was employed, with cobalt as the internal standard (GAMBLE and JONES, 1955). The samples were wet-ashed with 95 per cent sulphuric acid and heated in the muffle at 550°C. Calibration curves were previously made for the determination of Ni, V, Cr, Mn and Mo. Magnesium nitrate was used as an ashing aid and as a spectrographic carrier. Ultra-violet emission spectra were taken using a Hilger model E 492 spectrograph in the wavelength range from 2480 to 3500 Å, with a slit opening of 0·025 mm. Spectra were recorded on Ferrania photographic plates, calibrated

Table 3. Results of geochemical analyses

No.	Locality	Specific weight	Sulphur (%)	Oily comp. (%)	Resins (%)	Asphaltenes (%)	Carbenes (%)	Analysis of oily components C%	H%	S%	N%	C/H	M.W.
1	Tres 1	1·0187	6·10	55·62	24·06	19·91	0·41	81·70	11·44	5·61	tr.	7·14	520
2	Tres 2	1·0297	7·44	52·75	24·47	20·67	2·11	81·08	11·32	5·87	tr.	7·16	506
3	Cortaccia	1·0193	4·38	59·67	39·22	0·75	0·36	80·98	10·92	3·25	tr.	7·42	398
4	Mollaro 1	1·0390	3·39	48·29	34·79	16·80	0·12	84·10	12·73	3·12	tr.	6·60	550
5	Mollaro 2	1·0689	2·33	46·00	38·45	14·90	0·65	82·28	12·50	2·26	tr.	6·58	600
6	Zambana	1·0206	4·52	57·20	41·40	1·36	0·04	74·27	9·64	3·88	tr.	7·70	355
7	Valle dei Tovi	1·0404	3·90	53·83	43·82	2·31	0·04	78·02	10·60	3·06	tr.	7·36	388
8	Cavedine	1·0184	1·79	78·32	17·80	3·58	0·30	83·71	12·08	1·44	tr.	6·93	428
9	Cortemaggiore	0·8390	0·10	95·34	4·44	0·22	tr.	87·28	11·67	0·19	tr.	7·48	293
10	Montechino	0·7903	0·07	99·93	0·07	tr.	tr.	86·35	12·77	0·002	tr.	6·93	270
11	Salsomaggiore	0·8635	0·30	96·64	3·11	0·25	tr.	86·89	12·25	0·33	tr.	7·09	329
12	Velleia	0·8012	0·14	99·50	0·50	tr.	tr.	86·66	13·10	0·03	tr.	6·61	263
13	Vallezza (900 ft)	0·7625	0·09	99·70	0·30	tr.	tr.	85·15	13·06	0·13	tr.	6·52	265
14	Vallezza (2700 ft)	0·7592	0·05	99·50	0·50	tr.	tr.	85·67	13·08	0·02	tr.	6·55	305
15	Vizzola	0·8806	0·20	96·34	3·64	0·02	tr.	87·50	12·06	0·12	tr.	7·25	318
16	Salsominore	0·8522	0·48	95·14	4·12	0·74	tr.	86·10	13·18	0·33	tr.	6·53	336
17	Pavullo	0·7546	0·13	85·87	14·13	ass.	ass.	85·22	13·88	0·15	tr.	6·14	210
18	Pietramala	0·8893	0·09	98·29	1·71	ass.	ass.	87·63	11·44	0·27	tr.	7·66	300
19	Selvapiana	0·7865	0·22	99·72	0·28	ass.	ass.	86·06	12·98	0·20	tr.	6·63	295
20	Perticara	1·0286	10·50	76·64	14·10	9·13	0·13	78·77	10·71	10·38	tr.	7·35	430
21	Alanno (C 12)	0·9664	4·70	79·83	10·65	8·54	0·98	84·43	11·00	4·22	tr.	7·68	380
22	Alanno (C 1)	0·8520	2·90	94·95	4·59	0·46	ass.	83·82	12·50	2·64	tr.	6·70	286
23	Alanno (C 20)	0·8545	2·88	94·53	5·08	0·30	0·09	84·80	12·30	1·40	tr.	6·89	295
24	Alanno (C 18)	0·9417	4·09	85·68	10·39	3·78	0·15	84·80	11·91	3·10	tr.	7·12	310
25	Alanno (C 2)	1·0912	8·73	43·92	21·76	33·95	0·37	81·87	10·39	7·14	0·02	7·88	485
26	Scafa	1·2768	9·84	37·90	20·68	41·17	0·25	81·16	10·20	7·51	0·06	7·96	493
27	S. Spirito	1·0745	8·49	53·59	13·12	32·45	0·84	82·96	10·21	6·10	tr.	8·10	403
28	Tocco Casauria	0·9292	5·40	80·58	12·90	6·42	0·10	83·20	11·24	4·54	tr.	7·40	355
29	S. Potito	1·2452	7·56	36·38	16·42	45·58	1·62	81·70	10·20	7·16	0·02	8·01	532
30	Celano	1·2553	8·28	32·30	24·23	41·94	1·53	83·34	10·47	6·16	0·05	7·96	508
31	Casalbordino	0·9953	4·91	70·90	11·05	12·00	1·05	84·31	11·17	4·01	tr.	7·37	391
32	Petacciato	0·9994	1·31	59·92	13·83	21·62	4·63	85·76	12·56	0·90	tr.	6·83	378
33	Filettino	1·2736	11·37	22·97	16·05	60·07	0·91	82·58	10·17	7·18	0·05	8·12	547
34	Alatri	1·1279	8·21	28·50	18·50	52·85	0·15	79·39	9·85	8·12	0·11	8·06	540
35	S. Giov. Incarico	0·9887	4·70	85·30	9·90	4·69	0·11	84·54	11·09	4·14	tr.	7·62	321

with a seven-step rotating sector. The arc excitation was obtained from a multi-source power unit. The positive electrode of the arc was filled with a mixture of 10 mg ash and 10 mg graphite powder. The following analytical lines were chosen for this study: Mn 2575 Å (compared with Co 2521 Å); Cr 3015 Å; Ni 3051 Å; Mo 3170 Å and V 3185 Å (compared with Co 3044 Å). An Optica densitometer was used to measure the intensity of the lines. The calculation of trace-element concentration from photometric data was made with a Respektra calculator.

Reagents

Solvents for extraction and chromatography: "Aalar" type, British Drug House, Ltd. These were all carefully distilled prior to use and analytically controlled by gas chromatography and refractometry to verify the absence of non-volatile hydrocarbon impurities. Fuller's Earth: Clarsil PC, C.E.S.A., 100–200 mesh, activated by heating at 180°C for 24 hr. Sulphuric acid: Merck (d = 1·84), pro-analysis. Cobalt sulphate: Prepared by reaction of sulphuric acid with cobalt

Table 3—(*contd.*)

No.	Locality	Specific weight	Sulphur (%)	Oily comp. (%)	Resins (%)	Asphaltenes (%)	Carbenes (%)	Analysis of oily components C%	H%	S%	N%	C/H	M.W
36	Baranello	1·0398	5·23	46·13	30·28	20·41	3·15	83·74	10·30	4·98	0·21	8·13	460
37	Mutria	1·0350	5·35	55·51	25·25	17·92	1·32	83·10	10·80	4·57	0·06	7·70	384
38	Colle Sannita	1·1101	5·51	26·93	43·43	19·16	10·48	83·62	10·99	4·04	0·20	7·60	446
39	Ginestra Schiav.	0·9880	4·14	76·80	18·06	5·00	0·14	85·11	10·95	3·80	0·09	7·67	340
40	Pietrelcina	1·0270	5·34	66·15	22·15	11·45	0·25	83·95	11·10	4·05	0·20	7·56	400
41	Lapio	1·0352	6·61	66·77	13·21	19·63	0·39	82·49	10·21	5·74	0·10	8·08	442
42	S. Angelo Lomb.	1·1074	7·64	48·51	18·19	35·18	8·12	81·77	9·60	6·01	tr.	8·51	450
43	Serino	1·0360	7·07	50·15	27·01	17·37	5·47	83·43	11·10	5·06	0·10	7·52	404
44	Solofra	1·1510	10·10	15·10	13·00	60·11	11·79	81·10	9·77	7·89	tr.	8·30	489
45	Ospedaletto	1·0410	8·32	35·56	39·44	14·93	10·07	82·94	10·75	4·40	0·10	7·71	380
46	Paestum	1·0402	5·95	52·89	19·02	28·00	0·09	83·35	11·69	4·50	tr.	7·13	378
47	Corleto Monforte	1·0245	0·65	59·23	23·09	10·64	7·04	83·96	10·75	4·41	tr.	7·81	390
48	Tramutola	0·9758	3·99	78·43	16·94	4·46	0·17	84·78	11·14	3·54	tr.	7·61	397
49	S. Martino d'Agri	1·0590	3·30	58·10	26·89	10·21	4·80	82·92	11·43	2·70	tr.	7·25	400
50	Latronico	1·0620	5·43	51·72	34·85	13·10	0·33	85·30	10·61	3·80	0·10	8·03	447
51	Oriolo	1·0202	4·66	68·28	19·32	11·99	0·41	85·40	11·01	3·36	0·10	7·74	348
52	Albidona	1·0268	0·49	64·62	20·79	11·55	3·04	86·46	11·94	1·41	tr.	7·24	338
53	Marineo	1·0602	9·57	27·19	33·98	38·79	0·04	79·58	10·44	6·51	0·12	7·62	459
54	Ponte Bagni	1·0730	8·22	26·63	27·25	42·89	3·23	78·96	10·81	7·20	tr.	7·30	590
55	Petralia	0·9489	5·38	93·42	6·58	—	—	84·73	11·93	1·58	0·10	7·12	291
56	Avanella	0·7958	0·19	92·92	7·08	—	—	85·81	13·61	0·11	tr.	6·30	281
57	S. Giorgio	n.d.	0·48	73·01	24·67	2·18	0·14	84·74	12·97	0·20	tr.	6·53	380
58	Nicosia	0·9760	1·01	59·19	39·43	1·07	0·31	85·17	12·37	0·74	0·10	7·20	399
59	S. Agrippina	0·9352	1·68	95·79	4·21	—	—	86·22	12·11	1·44	0·05	7·12	341
60	Bivona	0·8857	0·44	94·80	5·20	—	—	86·00	13·23	0·29	0·05	6·50	335
61	Barrafranca	0·8677	0·42	89·32	10·68	—	—	84·77	13·41	0·33	0·06	6·32	240
62	Gela	1·0290	7·67	37·51	33·29	28·36	0·83	82·65	11·05	6·81	0·05	7·48	424
63	Vittoria	1·0142	6·49	51·67	28·09	20·23	0·01	82·81	11·70	6·09	0·05	7·07	407
64	Ragusa	1·0246	3·16	57·86	22·29	19·98	0·87	85·12	11·48	2·68	0·05	7·41	452
65	Ragusa	0·9380	2·40	73·33	12·01	11·72	0·29	85·85	12·38	1·46	0·06	6·93	392
66	Castelluccio	1·0246	2·34	61·55	26·84	11·61	tr.	86·16	11·58	1·23	0·05	7·44	432
67	Noto	0·9882	3·95	64·41	18·07	19·44	0·06	85·02	11·45	3·79	0·08	7·42	411
68	Fortugno	1·0319	2·60	54·94	19·55	24·50	1·01	85·92	11·89	2·18	tr.	7·22	420
69	Streppenosa	1·0346	2·22	58·58	24·44	10·53	6·45	84·91	11·53	0·72	0·09	7·36	467
70	Streppenosa	1·0209	2·35	65·66	20·54	12·85	0·95	86·10	11·54	1·19	0·06	7·46	408

oxide (Co_3O_4), spectrographically standardized, Johnson and Matthey. Magnesium nitrate: Merck, c.p., 0·20 g per ml of absolute ethanol.

Experimental Data

The data from geochemical fractionation work, using the methods indicated in Fig. 2, are given in Tables 3 and 4. The data from trace-metals spectrographic determinations are reported in Table 5.

Eastern Alps and Adige Valley area

All the shows analysed were collected from Triassic or Cretaceous carbonate formations. Seven of them are surface shows, while the other (Tres 2) is a subsurface asphalt show from a dry well. The Mollaro 1 show is generally considered to be an oil shale, although the complete solubility of its organic matter in chloroform and the analytical data have indicated its asphaltic nature and its association with petroleum.

The diagrams of Fig. 3 report the structural constitution of oily components

and the degree of alteration of each show, in terms of the contents in oily components, resins, asphaltenes + carbenes. The following observations can be made:

(a) The two shows from Mollaro, one of which was believed to be an oil shale, are similar in structure and in degree of alteration.

(b) The structure of the two Tres shows is slightly more naphthenic and the asphaltene content is higher than that of the Mollaro shows.

(c) The shows from Cortaccia, Valle dei Tovi and Zambana are almost entirely constituted by oily components and resins, and the nature of oily components is of the naphthenic type.

Table 4. Analysis of chromatographic fractions from three Sicilian shows

No.	Locality	Fractions	% Fraction in show	Elementary analysis of fractions					
				C%	H%	S%	N%	O%	C/H
62	Gela	White oils	26·25	83·39	11·69	4·88	tr.	0·04	7·13
		Dark oils	14·31	77·98	9·51	8·67	tr.	3·84	8·20
		Resins	13·70	71·08	8·75	7·09	tr.	13·08	8·12
		Asphaltenes	38·24	78·86	7·82	10·27	tr.	3·05	10·08
63	Vittoria	White oils	40·50	85·13	11·95	2·88	tr.	0·04	7·12
		Dark oils	16·06	80·39	9·66	5·72	tr.	4·23	8·32
		Resins	16·52	76·67	9·55	6·01	tr.	7·77	8·03
		Asphaltenes	22·99	78·04	8·76	10·19	tr.	3·01	8·90
65	Ragusa	White oils	44·50	86·56	11·97	1·45	tr.	0·02	7·23
		Dark oils	24·06	82·95	10·19	3·07	tr.	3·79	8·14
		Resins	16·52	79·84	9·73	3·26	tr.	7·17	8·20
		Asphaltenes	13·99	81·32	8·54	5·22	tr.	4·92	9·52

(d) The Cavedine show is the least altered in this area and its hydrocarbon-group position is similar to that of the Mollaro shows.

Infra-red spectra were run on the oily components from all these shows. The spectra of the two Mollaro shows are identical; they show a remarkable similarity to those of the Tres and Cavedine shows (see Fig. 4(a)). The band at 5·85 μ indicates the presence of carbonyl structures, and attests to a moderate degree of oxidation of these shows. The 8·55 μ band, well delineated in these spectra, is due to the presence of branched hydrocarbon structures. The band at 13·95 μ, representing aliphatic chains, is slightly stronger in the Cavedine show than in the shows of Tres and Mollaro: this is probably connected with the lower degree of alteration indicated by the geochemical analysis.

The infra-red spectra of oily components from the shows of Cortaccia, Valle dei Tovi and Zambana, represented in Fig. 4(b), are very similar to each other: they show an exceptionally high degree of oxidation, as indicated by the strong bands at 5·75–5·85 μ; 7·70–8·00 μ; 8·80–8·95 μ. The strong aromatic character of these three shows is indicated by the strong bands at 13·50 μ and 14·30 μ. The combination of an exceptionally high degree of alteration with a relatively low molecular weight of oily components is rather unusual. Besides, the presence of a band

Table 5. Results of quantitative spectrographic analyses

No. (see Table 1)	Locality	Nickel (p.p.m.)	Vanadium (p.p.m.)	Chromium (p.p.m.)	Molibdenum (p.p.m.)	Manganese (p.p.m.)	Ni_V
20	Perticara	11·3	5·0	2·0	13·5	0·7	2·26
21	Alanno (C 12)	30·0	55·0	2·5	19·5	<0·1	0·54
22	Alanno (C 1)	2·6	6·8	0·5	0·2	<0·1	0·38
23	Alanno (C 20)	2·2	5·4	0·2	0·4	<0·1	0·41
24	Alanno (C 18)	10·6	26·2	1·3	3·5	0·1	0·40
25	Alanno (C 2)	106·0	229·0	10·1	90·5	1·5	0·46
26	Scafa	109·0	248·0	9·1	82·0	1·4	0·44
27	S. Spirito	25·0	45·0	8·1	75·0	0·3	0·55
28	Tocco Casauria	15·5	36·0	1·5	3·0	<0·1	0·43
29	S. Potito	81·5	186·5	10·7	27·0	0·1	0·44
30	Celano	90·0	210·0	9·1	15·2	0·2	0·43
31	Casalbordino	57·5	95·0	3·1	3·2	1·4	0·60
32	Petacciato	15·4	59·5	8·2	0·5	8·5	0·26
33	Filettino	154·0	196·0	1·2	171·0	0·3	0·78
34	Alatri	155·0	229·0	10·0	183·0	0·2	0·68
35	S. Giovanni Incarico	15·1	25·1	1·1	5·0	<0·1	0·60
36	Baranello	29·7	82·5	5·0	1·0	2·0	0·36
38	Colle Sannita	32·7	73·0	1·0	2·0	9·7	0·45
39	Ginestra degli Schiavoni	6·6	12·8	2·0	0·5	0·5	0·52
40	Pietrelcina	68·2	63·5	2·4	0·2	0·2	1·07
41	Lapio	30·2	38·7	2·5	4·8	0·	0·78
48	Tramutola	7·1	5·6	<0·2	<0·2	<0·7	1·27
51	Oriolo	13·7	36·0	1·4	0·5	0·3	0·38
53	Marineo	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
54	Ponte Bagni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
55	Petralia	0·9	0·1	0·4	0·7	<0·1	9·00
56	Avanella	0·3	0·1	0·3	<0·2	<0·1	3·00
57	S. Giorgio	5·2	2·0	0·9	0·8	0·6	2·60
58	Nicosia	90·0	149·1	5·9	4·8	0·5	0·60
59	S. Agrippina	1·5	0·2	0·3	<0·2	<0·1	7·50
60	Bivona	3·8	0·8	0·2	<0·2	<0·1	4·75
61	Barrafranca	1·2	2·1	<0·2	<0·2	0·8	0·57
62	Gela	94·5	147·0	5·0	8·4	0·5	0·64
63	Vittoria	90·1	39·1	2·0	4·2	0·2	2·30
64	Ragusa	84·0	14·1	0·5	1·3	0·4	5·95
65	Ragusa	41·0	8·1	0·1	0·8	0·3	5·06
66	Castelluccio	76·0	13·9	0·2	1·2	0·2	5·46
67	Noto	97·5	21·5	1·0	2·6	0·8	4·53
69	Streppenosa	70·2	20·1	0·3	1·0	0·5	3·49

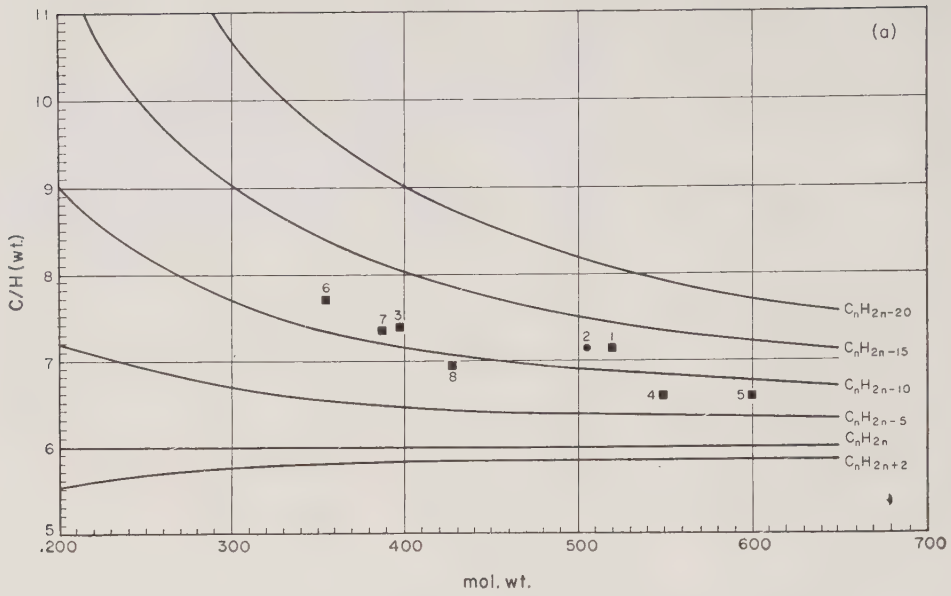

Fig. 3(a) Structural composition of oily components, Eastern Alps area.

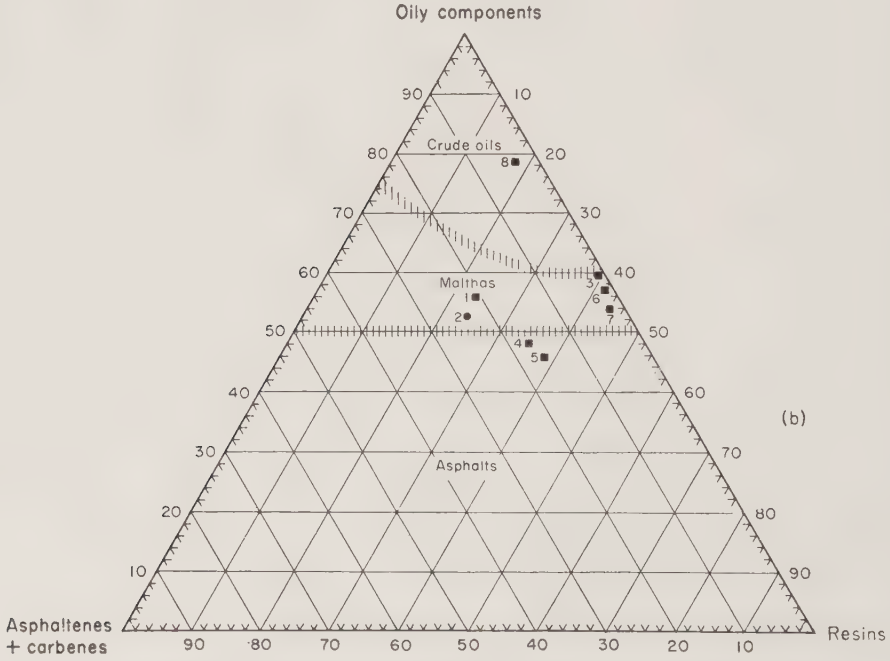

Fig. 3(b) Degree of alteration of shows, Eastern Alps area.

at 2·9 μ, which is attributed to N—H bands and that of two sharp bands at 6·25 and 6·32 μ due to an aromatic ring conjugated to a double bond, leads to the conclusion that the petroliferous significance of these shows is very doubtful. Further study is in progress to investigate this point.

Owing to the insufficient amount of each sample available for this study, trace-metal spectrographic determination was not carried out on the shows of this area.

Po Valley and Northern Apennine area

Twelve shows from this area were analysed: eleven of them are subsurface shows from oil wells, the other is an oil show from a sulphur mine. As indicated in Table 1, six of the shows were found in Miocene beds and six in inglobate olistoliths in the olistostroma.

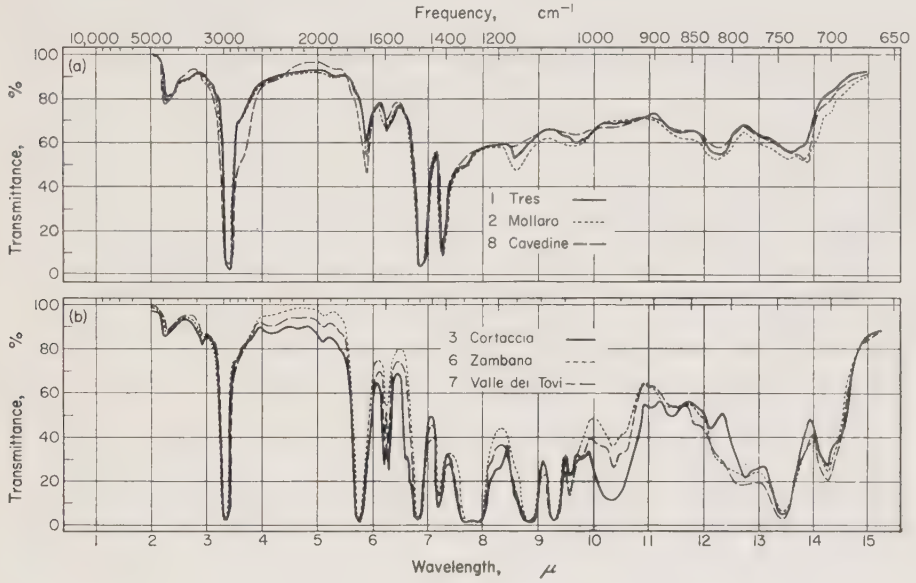

Fig. 4. Infra-red spectra of oily components of shows, Eastern Alps area.

The following deductions can be made from the geochemical data, represented graphically in Fig. 5:

(a) All the oils are remarkably light and not very altered: this is indicative of good trap efficiencies and consequently of only weak contacts with alteration agents.

(b) The oils from Cortemaggiore, Vizzola and Pietramala are definitely naphthenic and similar to each other both in structure and in degree of alteration. The oil from Salsomaggiore is similar to them but its naphthenic character is less evident. The oils from Montechino, Velleia, Vallezza, Salsominore, Pavullo and Selvapiana are of much more paraffinic nature.

(c) The oil from the sulphur mine of Perticara is of mixed-naphthenic nature. Its sulphur content is remarkably high.

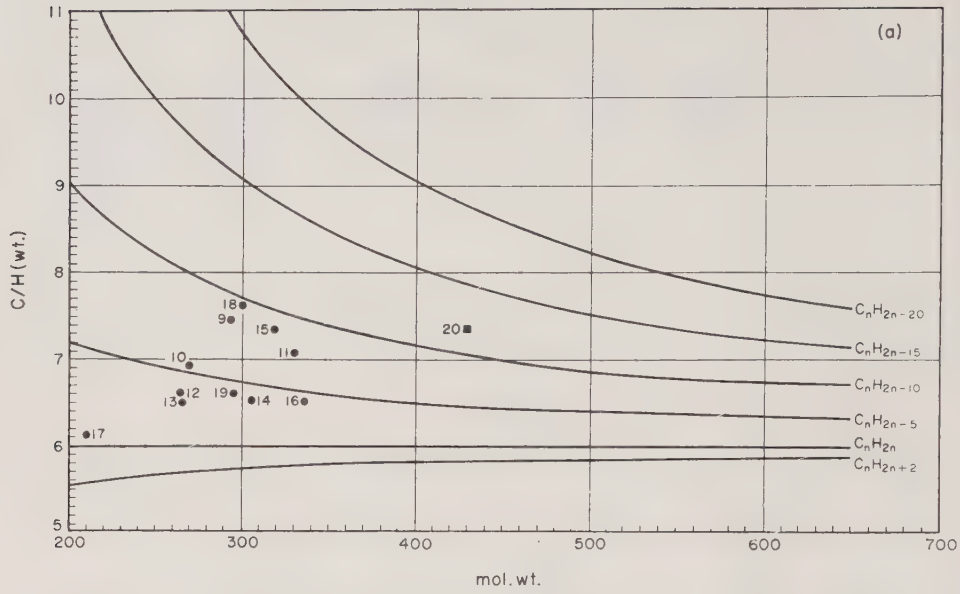

Fig. 5(a) Structural composition of oily components, Po valley and Northern Apennine area.

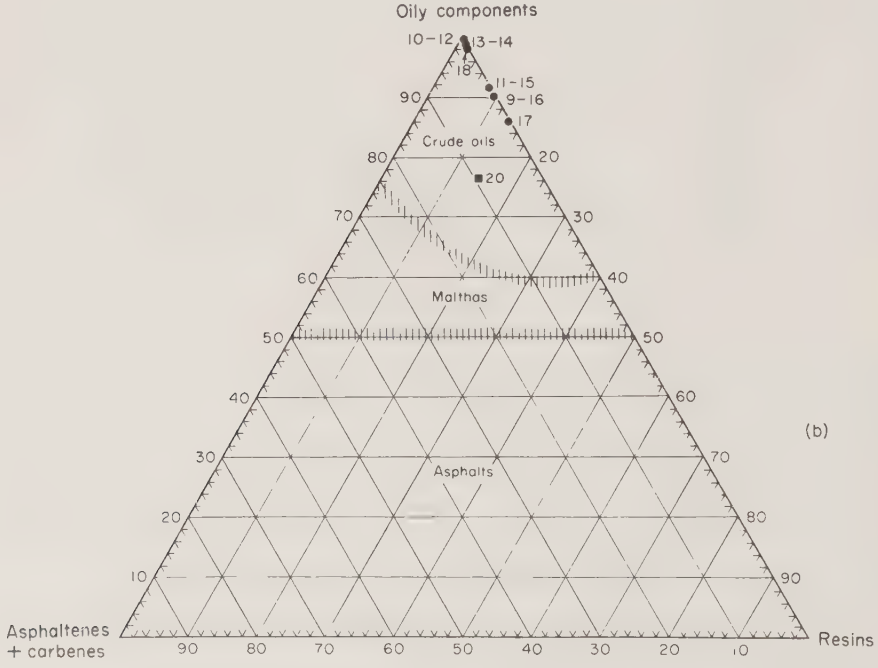

Fig. 5(b) Degree of alteration of shows, Po valley and Northern Apennine area.

(d) The majority of the oils from olistostroma appear to be paraffinic: this suggests a mechanism of selective filtration of paraffinic hydrocarbons through the "Argille scagliose". The fact that the olistostroma oil from Pietramala is naphthenic is to be attributed to the close contact of the reservoir rock with the underlying autochthonous formations: the selective filtration of paraffinic hydrocarbons through the olistostroma would be inefficient here because of the relative thinness of olistostroma.

It may also be noticed that two of the paraffinic oils come from autochthonous formations (Salsominore and Selvapiana).

The infra-red spectra of the oily components of the shows from Cortemaggiore, Vizzola and Pietramala are shown in Fig. 6(a). The aromatic structure and the

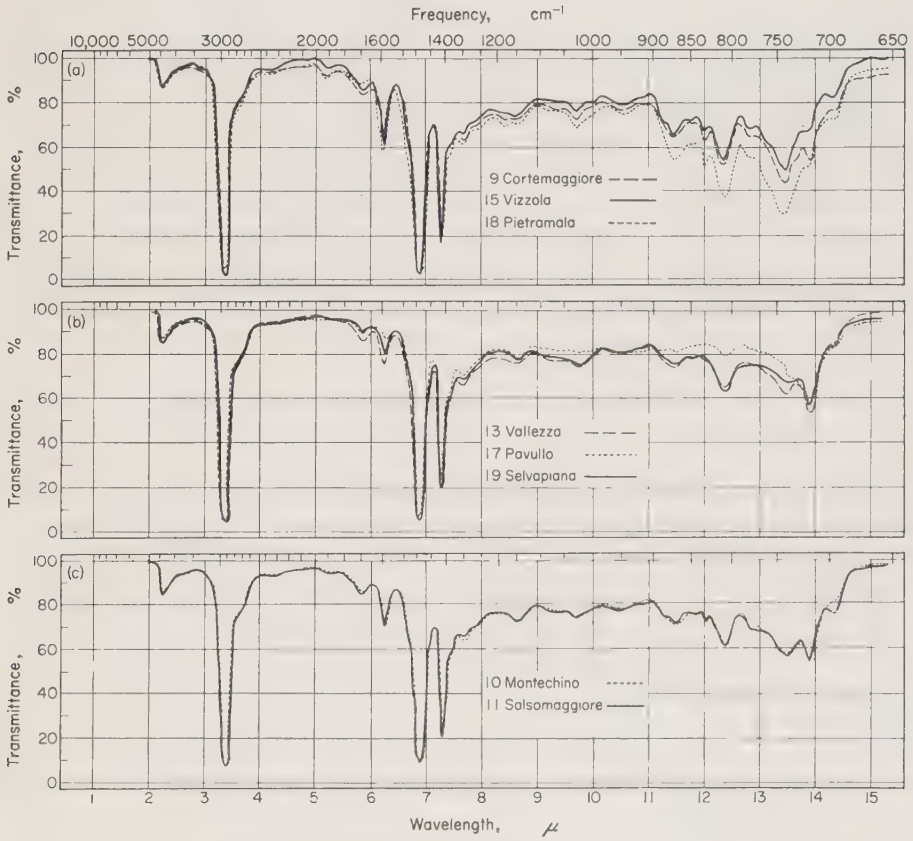

Fig. 6. Infra-red spectra of oily components of shows, Po valley and Northern Apennine area.

similarity of the nature of such oils is evident from the bands at 6·25 μ; 11·48 μ; 12·37 μ; 13·50 μ and 14·32 μ. The weakness of the CO band at 5·85 μ attests to the low content of molecules possessing ketonic structures.

In Fig. 6(b) the infra-red spectra of the oily components from the Vallezza, Pavullo and Selvapiana shows are reported. The similarity of these spectra is very

remarkable. The spectra of the Salsominore and Velleia oily components, which are not shown on this graph, are very similar to these. The paraffinic nature of such oils is evident from the bands at 8·70 μ and 13·87 μ. The aromatic bands, present in the oils of the former group, are here greatly decreased in intensity.

The infra-red spectra of the Salsomaggiore and Montechino oily components (Fig. 6(c)) indicate that the structure of such oils is intermediate between that of the naphthenic oils and that of the paraffinic oils listed above.

The presence of these two oils with intermediate structures, whose infra-red spectra indicate certain similarities of pattern with both the groups listed above, leads to the hypothesis that all the oils of this area are correlative with each other and that the structural differences may be attributed to environmental factors.

The oil from the Perticara sulphur mine has a substantially paraffinic structure and its oily components are similar in constitution to those of the Selvapiana show. In the infra-red spectra, however, a rather strong band at 12·55 μ is present, which may be attributed to sulphur-containing ring structures. This is related to the high sulphur content of this oil.

Central Apennine area

The shows of this area are oils and asphalts from formations ranging in age from Triassic to Miocene. Nine of them are sub-surface shows from the Abruzzi oil fields: the Cigno field (indicated with the letter C in Table 1) is represented by five shows from carbonate formations ranging from Middle Miocene to Cretaceous. Six are outcropping asphalts, two of which (Scafa and Santo Spirito) belong to the important asphalt mines of Abruzzi.

The results of the geochemical work are shown in Fig. 7. The data of trace-metals spectrographic determination are indicated in Table 5. The following observations can be made:

(a) The distribution of shows in the geochemical diagrams supports the idea of a close relationship among all these oils and asphalts. The oils from Lower Miocene reservoirs are the most paraffinic and the least altered shows in the area. The outcropping asphalt shows from Triassic and Cretaceous formations are the most altered, as indicated by the high asphaltene content and by the values of average molecular weights of oily components.

(b) The paraffinic character of Lower Miocene oils appears to be related to their sulphur content, which is the lowest among all the shows in the area. It may be pointed out that, in general, the sulphur content in the shows studied seems to increase with the average molecular weight of oily components and with the asphaltene content in the samples.

(c) The nickel /vanadium ratios of all the samples analysed from this area are very close to each other, even if the absolute values of the nickel and vanadium contents are variable depending on the degree of alteration of the shows and on the environmental conditions. No other trace-metals correlation was possible, because the contents of other trace metals studied showed irregular variations without any apparent relationship to the degree of alteration of the shows or to the properties of the host formations.

The infra-red spectra of the oily components from the shows of Alanno (Lower

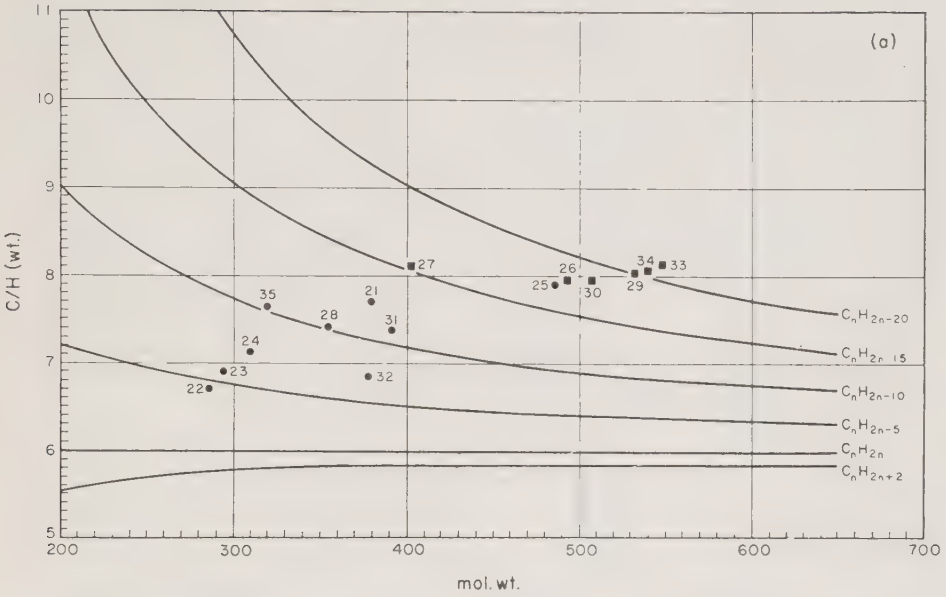

Fig. 7(a) Structural composition of oily components, central Apennine area.

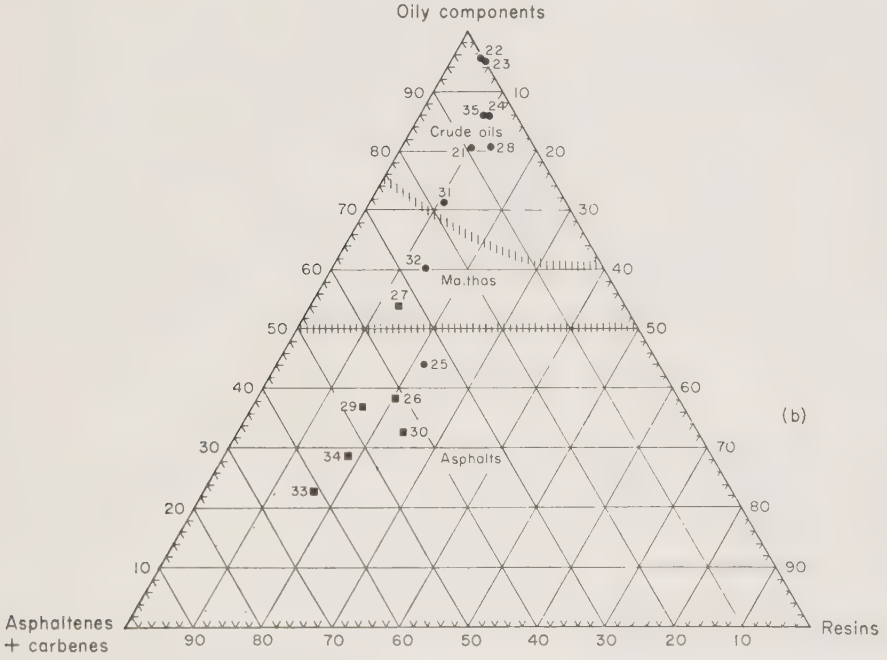

Fig. 7(b) Degree of alteration of shows, central Apennine area.

Miocene), Casalbordino and Petacciato are represented in Fig. 8(a). Their paraffinic structure is evident by the strong band at 13·90 μ. The oxidation is very low in the oils from Alanno and Casalbordino, while the sharp band at 5·87 μ in the oily components from Petacciato indicates the presence of CO groups.

The bands of aromatic structures at 12·37 μ and 13·50 μ are more pronounced in the spectra of Fig. 8(b), representing the oily components from the shows of Alanno (Middle Miocene), San Potito and Filettino. In these oils the paraffinic

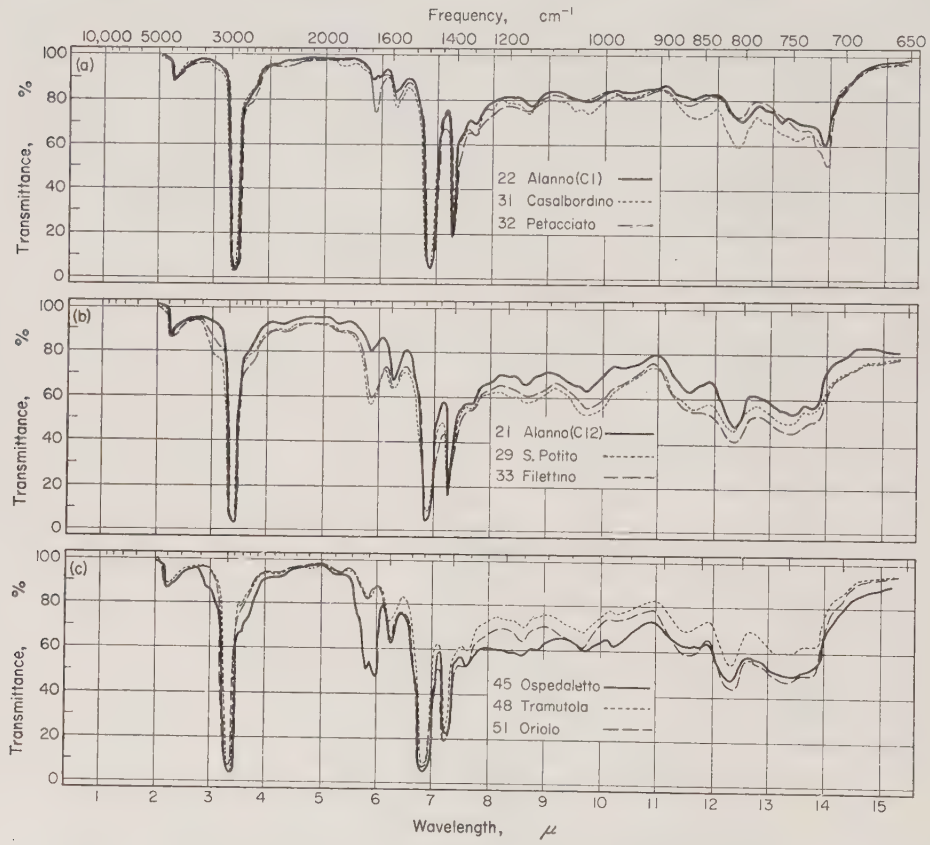

Fig. 8. Infra-red spectra of oily components of shows, central and southern Apennine area.

band at 13·90 μ is much weaker. The high degree of oxidative alteration, shown by the strong band at 5·84 μ, is evident in the oily components from the outcropping asphalts of S. Potito and Filettino. In spite of the differences in the age of the host rocks, these three shows exhibit very close structural similarities in their oily components.

The results of geochemical fractionation work and those of trace-metals determinations are in favour of the hypothesis of a close relationship of all the shows from this area. The differences in the structures of oily components are due most probably to environmental factors both during the migration of the oils and after their entrapment.

Southern Apennine area

All the shows from this area, with the exception of the oil from the small field of Tramutola, are outcropping asphalt or oil shows. Ten of these shows are from olistostroma, the remaining seven are from autochthonous formation, ranging in age from Jurassic to Miocene.

The following deductions can be made from the data of geochemical work, given in Table 3 and reported graphically in Fig. 9:

(a) There is a strong similarity in the structure of the oily components of all the shows from this area. It is a remarkable fact that this similarity is extended to the oily components of the shows from the Central Apennine area. All the oily components have a more or less pronounced naphthenic structure, which is probably related to their high sulphur content.

(b) The shows from olistostroma have the same naphthenic character as those from autochthonous formations. This may be attributed to a cyclization of more paraffinic oils to give naphthenic asphalts, as a consequence of the action of atmospheric agents (Bienner *et al.*, 1955).

(c) The Ni/V ratio of the oils and asphalts from this area are in general similar to the values found for the shows from Central Apennine area. Only the oils from Tramutola and Pietrelcina have a Ni/V ratio greater than 1: this deviation from the provincial character of this trace metals distribution is not very strong quantitatively and it may be due to particular environmental factors either during or after the entrapment of these oils.

The infra-red spectra of the oily components of the shows from this area are all remarkably similar to each other, with only some minor variations due to the degree of oxidation (CO bands at 5·75 μ and 5·84 μ) and to the presence, in some of these oily components, of a band at 6·00 μ which may be attributed to carbonyl derivatives probably formed by surface-alteration processes. The spectra of the oily components from Ospedaletto, Tramutola and Oriolo are presented in Fig. 8(c). The similarity of the structure of such oily components to those of Fig. 8(b), from shows of the Central Apennine area, is very significant. Apart from the presence, in the Ospedaletto oily components, of the carbonyl derivatives band at 6·00 μ, and that of a weak band at 10·25 μ, probably due to cyclo-paraffinic groups, there are practically no differences in the structures of the oily components from the shows of this wide area.

Sicily

Seven sub-surface shows and eleven surface shows of oils and asphalts were studied. Four of the outcropping shows are from olistostroma, whilst all the other shows are from autochthonous formations, ranging in age from Triassic to Middle Miocene.

The geochemical data, given in Table 3, are graphically represented in Fig. 10. The following observations can be made:

(a) All the shows from south-eastern Sicily appear to be closely interrelated. The structure of their oily components is mixed-naphthenic or naphthenic, the degree of naphthenicity increasing with the sulphur content of oily components and with their average molecular weight. The Ragusa oil, whose sulphur content

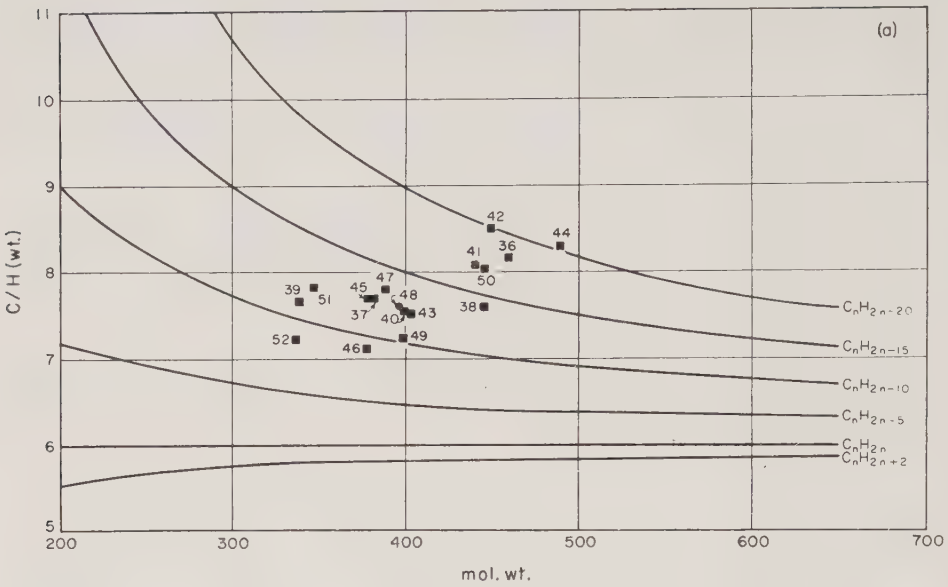

Fig. 9(a) Structural composition of oily components, southern Apennine area.

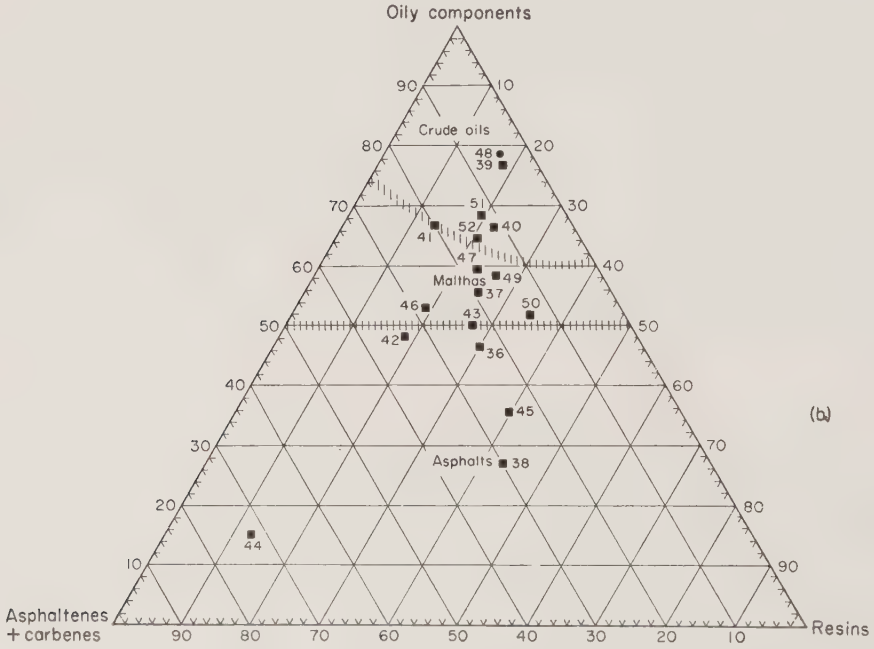

Fig. 9(b) Degree of alteration of shows, southern Apennine area.

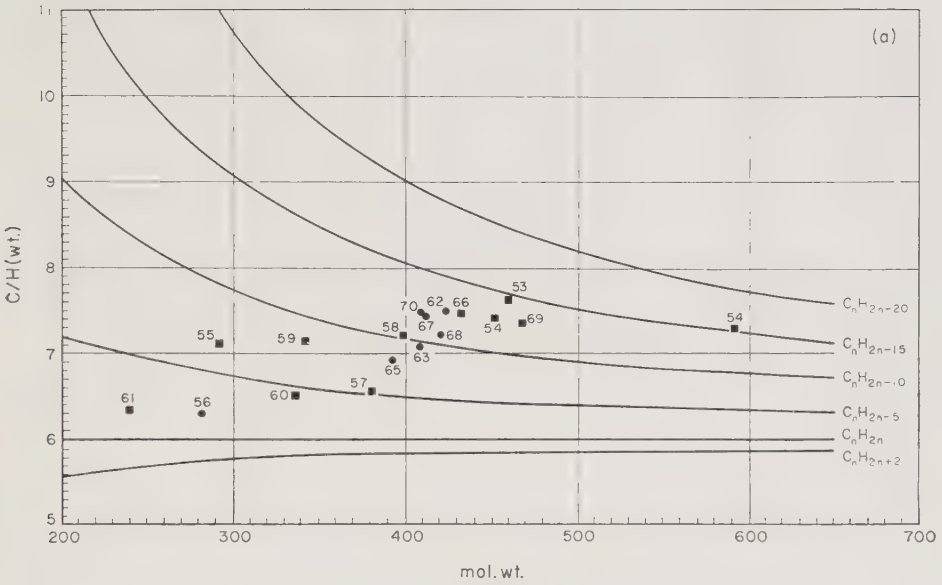

Fig. 10(a) Structural composition of oily components, Sicily.

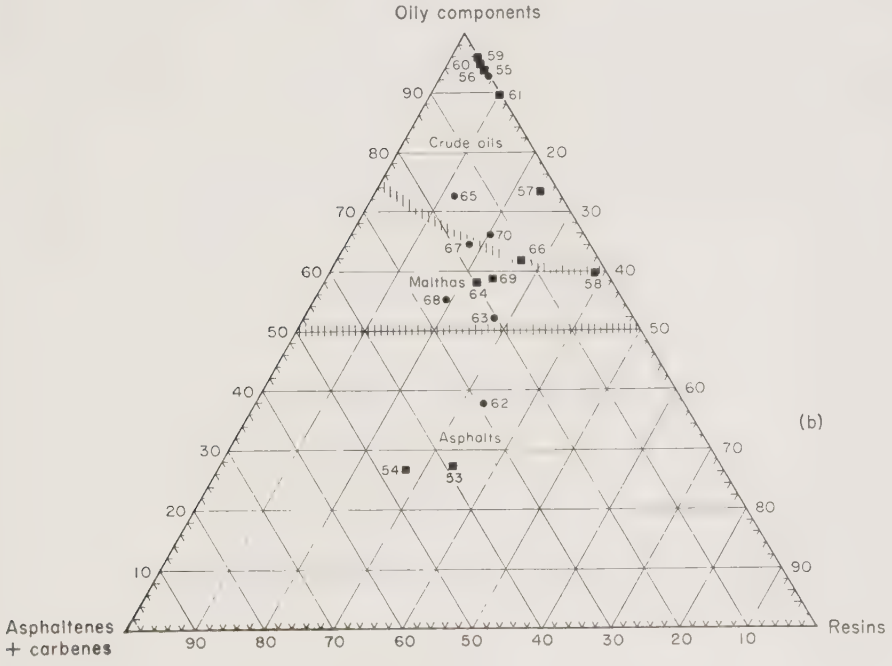

Fig. 10(b) Degree of alteration of shows, Sicily.

is the lowest among the shows studied from south-eastern Sicily, is also the least naphthenic and the least altered among these shows. The asphalt from Gela, characterized by a very high sulphur content, is much more naphthenic and more altered (higher molecular weight of oily components, higher content of asphaltenes), while that from Vittoria is intermediate between these two, in agreement with the sulphur content.

(b) Several other oils and asphalts from different parts of Sicily, such as the asphalts from Marineo, Ponte Bagni, Nicosia and the oils from Petralia and S. Agrippina, are very similar in structure to the shows of the group of south-eastern Sicily. The asphalts from Ponte Bagni and Marineo, in western Sicily, are the most altered shows in the whole group. The degree of alteration seems to decrease going towards the east.

(c) The oils from Avanella, Bivona and Barrafranca, and the asphalt from S. Giorgio, have a pronounced paraffinic structure and appear to be interrelated. Two of these shows (Bivona and S. Giorgio) are from olistostroma; the other two are from autochthonous formations.

(d) The trace-metals spectrographic determination indicates that the concentrations of trace metals are in general low in the group of paraffinic shows and high in the group of mixed-naphthenic and naphthenic shows. However, two oils from this latter group (Petralia and S. Agrippina) have low trace-metals concentrations: this could be related to paleogeographic trends (Bonham, 1956). A differentiation of the paraffinic oils from the naphthenic oils on the basis of the values of the Ni/V ratio does not appear to be possible, since the oils fromAvanella and Bivona and the asphalt from S. Giorgio have Ni/V ratio values very similar to those of the naphthenic oils group. The Ni/V ratio in the oil from Barrafranca and in the asphalts from Gela and Nicosia diverges from the average values, which are of the order of 3 to 5.

The infra-red spectra of oily components from the Sicilian shows, indicate a close structural similarity among the oils from Ragusa, Noto, Streppenosa, Petralia, S. Agrippina, and the asphalts from Ragusa, Castelluccio, Streppenosa, Fortugno, Nicosia. In Fig. 11(a) the infra-red spectra of the oily components from the Ragusa and Petralia oils and from the Ragusa asphalt are reported.

The spectra of the oily components of the asphalts from Ponte Bagni, Marineo and Gela (the latter two are reported in Fig. 11(b) appear to be closely interrelated and show a certain degree of similarity with the spectra of the first group (Fig. 11(a). The higher degree of alteration of the Gela and Marineo oily components is evident from the lower transmittance in the wavelength range 8–14 μ. The band at 14·30 μ, attributed to simple aromatic structures, which is pronounced in the spectra of Fig. 11(a), is much weaker in the oily components from Gela and Marineo, which are characterized by a higher degree of condensation.

The infra-red spectrum of the oily components from the Vittoria asphalt presents an average transmittance, in the 8–14 μ range, intermediate between that of the Ragusa-type and of the Gela-type spectra. The intensity of the 14·30 μ band is slightly in the Vittoria than in the Gela oily components. These infra-red spectroscopic data corroborate the conclusion of geochemical work, that there is a gradual increase in the alteration of oils and asphalts, going from the Ragusa area to Vittoria and to Gela.

The spectra of the oily components of the Avanella and Bivona oils and of the S. Giorgio asphalt are shown in Fig. 11(c). The paraffinic nature of such oily components is evident from the presence of a very strong band at 13·90 μ, and from the weakness of the aromatic bands at 12·37 μ and at 13·50 μ. The oil from the sulphur mine of Barrafranca has a lower paraffinic character and its structure, as shown by infra-red data, is intermediate between those of the paraffinic oils and those of the oils of the Ragusa type.

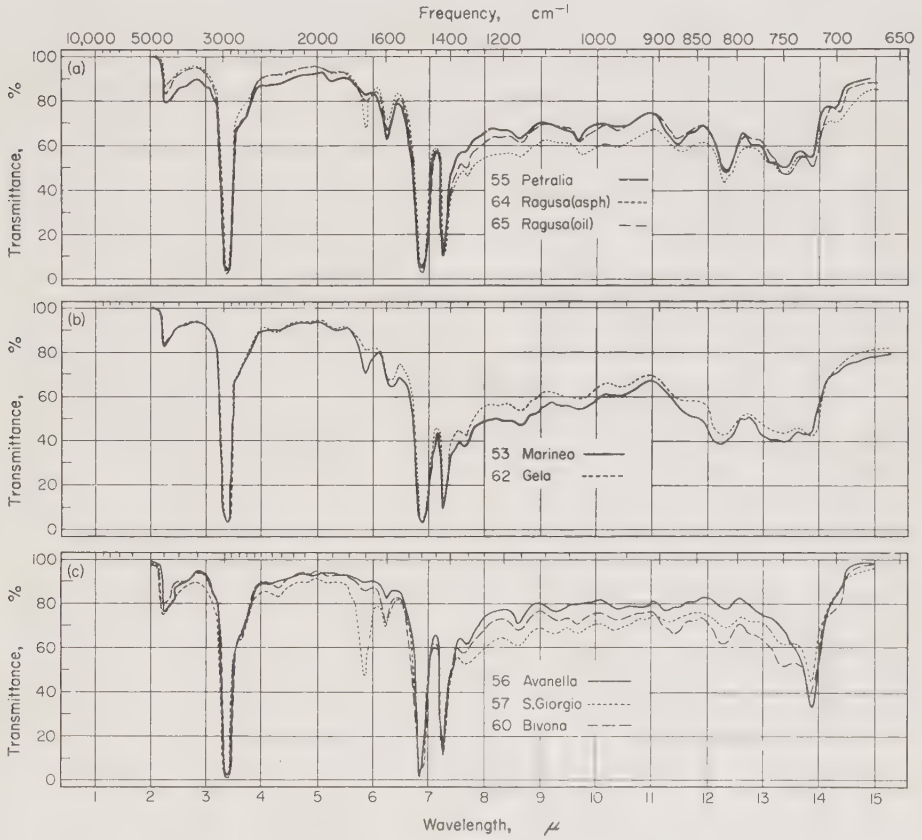

Fig. 11. Infra-red spectra of oily components of shows, Sicily.

Thus, the strong structural differences between the Gela-type oils (naphthenic) and the Avanella-type oils (paraffinic) are mitigated by the existence of oils with intermediated characters and with general similarities in band distribution in the infra-red spectra. This leads to the hypothesis that the structural differences among the various oils and asphalts in Sicily are due to the environmental rather than genetical factors.

In Table 4 the results obtained in the chromatographic fractionation of the Ragusa oil and of the Gela and Vittoria asphalts are reported, as well as the chemical analyses of white oils, dark oils, resins and asphaltenes. The oxygen

content is the highest in the resins fraction, while the sulphur content increases regularly from white oils to dark oils, resins and to asphaltenes. Asphaltenes are constituted by highly condensed products with the highest C/H ratio and a relatively low oxygen content.

Infra-red spectra were run on all these fractions in order to compare the structures of the altered fractions (Stewart, 1957): the spectra of these four fractions of the Ragusa oil are reported in Fig. 12 as an example.

The infra-red spectra of the white oils are generally similar to those of the oily components obtained with the Louis method, but the absence of oxygen-containing

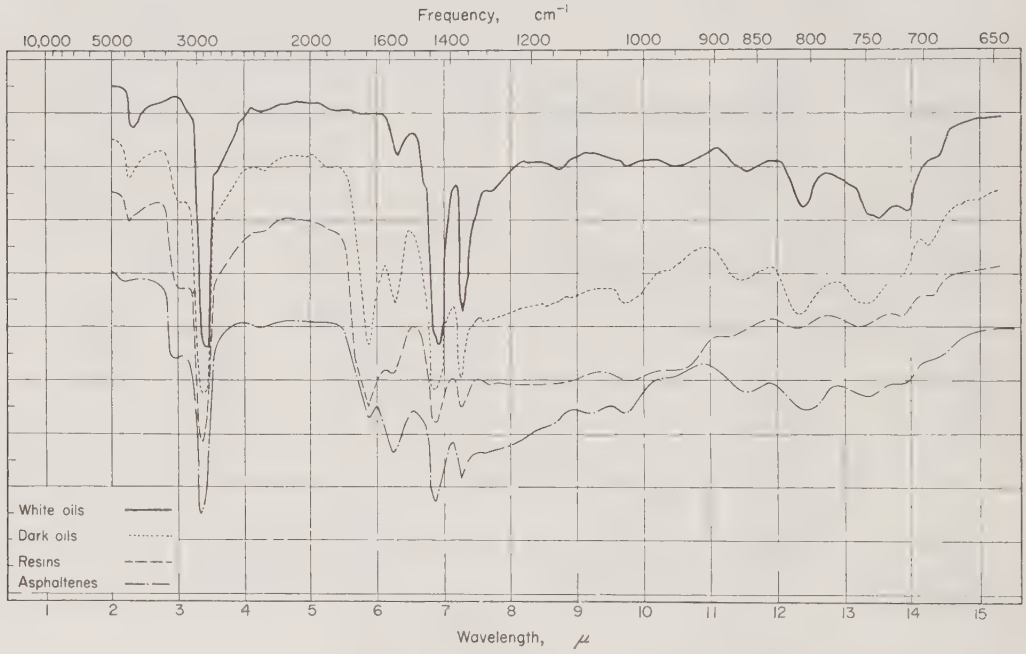

Fig. 12. Infra-red spectra of chromatographic fractions of Ragusa oil.

molecules in the white oils is always evident. A comparison of the structures of dark oils, resins and asphaltenes from different oils and asphalts indicates that the structural dissimilarities which are found in the oily components, are recurrent in the more altered fractions.

Discussion of Results

The petroliferous significance of the Mollaro shows has been evidenced. They have been correlated with other asphalt shows in the Eastern Alps area.

The oils of the Po Valley and Northern Apennine area have been subdivided into three groups, of naphthenic, intermediate and paraffinic structures. These oils are all remarkably light: the lightest being also the most paraffinic. The hypothesis of a mechanism of a selective filtration of paraffinic hydrocarbons

through the shaly sections (particularly through the "argille scagliose") is advanced to explain the structural differences found among the various oils of this basin. The mechanism of this selective filtration is in our opinion that of a chromatographic separation process. Both geometric configuration and polar character of organic molecules play a role in determining the relative mobility of the different components of an oil through shale beds. Linear paraffinic hydrocarbons, whose polar character is very low, are the most mobile substances in a crude oil.

Close structural similarities were found among all the oils and asphalts from the Central and Southern Apennine area. A gradual transition from light mixed-paraffinic oils to heavier naphthenic oils and asphalts is evident from geochemical work. The sulphur content appears to be related to the degree of molecular condensation and the intensity of alteration. The structural differences cannot be attributed to the different origins of the various oils and asphalts: environmental factors such as the leaching by the formation waters, the interaction with mineral sulphur (gypsum), the oxidative action of the atmosphere or of meteoric waters, are believed to be responsible for the structural differences found in this area. Sediments of Triassic or pre-Triassic age are believed to have been important sources of petroleum in this area. The high sulphur content, typical of all the shows studied from this area, may be attributed at least in part to the reaction of the oil with the shaly-gypsiferous formation of Triassic age.

The geochemical work has indicated that a definite correlation exists between the Ragusa oil and a number of oils and asphalts from Sicily. The asphalts from Ponte Bagni, Marineo and Gela have the highest sulphur contents and their oily components present a high degree of molecular condensation. The progressively growing alteration from the Ragusa oil to the related Vittoria and Gela asphalts leads to the hypothesis that this differentiation may be attributed to a leaching by the formation water, which would remove the most soluble and least alterated fractions.

Paraffinic oils were found in Sicily, either in olistostroma, or in autochthonous formations intercalated with shaly sections. The hypothesis of a selective filtration of paraffinic hydrocarbons through the shales can be advanced also in this case. Furthermore, the presence of the Barrafranca oil, whose structure is intermediate between the paraffinic oils and the Ragusa oil, supports the conclusion that there is no evidence for assuming different origins of the Sicilian oils.

Conclusions

If the geochemical and structural characteristics of oils from different basins are considered (for example, the oils from Cortemaggiore, Alanno, Tramutola and Ragusa), remarkable analogies are noticed. The structural dissimilarities among the oils within each basin could not be ascribed to their different origins. These results are in good agreement with the ideas on the relatively simple constitution of crude oils (Baker, 1958; Meinschein, 1958).

The structural dissimilarities among the oils within each basin have been attributed essentially to environmental factors. This supports the idea that a complex equilibrium existing in each basin determines the character of each oil,

according to the position of the oil within the basin and according to the relationship with the environment. Differentiations may occur as a consequence of: selective solubilization by the waters and selective unloading of the solutions; chemical and physicochemical interactions with the minerals, either during or after the migration; distribution of hydrodynamic potential; efficiency of entrapment.

The geochemical analysis represents a valuable tool for understanding the environmental conditions in different parts of a given basin, by the determination of the structure and degree of alteration of oils and asphalts in the basin. The validity of certain geochemical mechanisms of the oils, such as the selective filtration of paraffinic hydrocarbons through shales, or the behaviour of sulphur as a condensation and cyclization agent, should be supported by further experimental work.

The infra-red spectrographic analysis of oily components (and of altered products) is valuable for the structural study of oils and asphalts. Furthermore, the hydrocarbon-type structure may be calculated with good precision from spectral data during exploratory work, when only small amounts of oils are available (Brandes, 1956).

The integration of different methods of geochemical analysis is believed to be necessary for the understanding of the physicochemical factors affecting the entrapment and the alteration of oils.

Acknowledgements—The authors wish to acknowledge the contribution of M. P. Marchetti and E. Di Napoli, whose geological comments and criticism were of great help during this work.

Particular credit is due to C. A. Ceselli, M. Masoero and C. Tosi for obtaining the spectrometric data needed in this investigation; to the geologists who collected samples of the shows needed for this work and provided stratigraphic information; to the Managements of Gulf Italia Company, Agip Mineraria, Società Petrolifera Italiana, Società Petroli d'Italia, Società Idrocarburi Nazionali, Società Castelgrande, Società Petrosud, who provided oil samples for geochemical analysis.

Stimulating discussion were held with W. H. Roberts of Gulf Research and Development Company. It is a pleasure to acknowledge his extremely valuable ideas and comments.

Thanks are due to the Management of Montecatini Co. for the permission to publish this paper.

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A geochemical profile in the Baltic Sea*

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(*Received* 24 *October* 1960)

Abstract—An investigation has been made of the relationship between depositional environment and element distribution in sediments from the Baltic Sea. A prominent feature of the Baltic is its salinity stratification, which gives rise to changes in bottom character from oxygenation to stagnation as greater depths are approached.

Maximum heavy metal concentrations were not found in the central, most stagnant and organic-rich parts of the basins, but in the transition zone to stagnant conditions. Manganese–iron nodules were found in a peripheral area characterized by aerated bottom water but moderately reducing sediment environment, as measured by redox potential determinations. In two of the Baltic deeps manganese was found enriched in sapropelic sediments, in one case reaching 5·2 per cent MnO. The mineral responsible for the enrichment is regarded as a mixed manganese–calcium carbonate.

Introduction

The purpose of the larger investigation from which the present results have been taken was to examine the influence of depositional environment on the distribution of major and minor elements in sediments from the Skagerack to the Baltic Sea (see location map, Fig. 1). To obtain more quantitative evaluation of the environment, determinations of the hydrogen ion activity(pH) and the degree of stagnation, as measured by redox potential (EH), were made for both the sediment and the bottom water. Bottom water chlorinity and temperature were also determined, and in some cases other parameters were measured as well. The present paper will be restricted to a few of the interesting features shown by sediments in the central Baltic area.

Only a brief mention of the sampling and analytical techniques will be made here; the details will be presented in papers in preparation.

Sampling

The samples were taken in the summer of 1959 on an expedition of the Swedish hydrographic vessel, *Skagerak*, led by Professor B. Kullenberg. The sediments were obtained with 1 and 3m Kullenberg piston corers, while the bottom water for the stations described in this report was mainly obtained using Knudsen samplers. The distance of the water sampler from bottom varied somewhat, averaging 1–2 m in most cases, but the sampling technique was deemed adequate roughly to characterize the bottom water not in immediate contact with the sediment. The sediment reserved for later analysis represented approximately the upper 20 cm of the core unless otherwise stated. In cores of this type it is estimated that roughly from 1 to 2 per cent of the total length of the core was lost from the top by smearing along the tube.

* Paper read before the XII General Assembly of the International Union of Geodesy and Geophysics, Helsinki, 26 July–6 August 1960.

Fig. 1. Location map of stations in the Skagerack, Cattegat and Baltic Sea. Line *B–B'* is approximately 250 km.

Analytical Techniques

The following techniques were used in the element analyses.

Emission spectrography	X-ray fluorescence spectrography	Chemical	Fluorimetry
Si Ti Sr Co Cd	Fe	C S Th	U
Al K Ba V Ag	Mn	N F CO_2	
Fe Na Ge Mo As	Zn	H Fe H_2O	
Mn Rb Ga Pb Sn		P U	
Ca Li Cr Cu P			
Mg B Ni Zn			

The bulk of the work was carried out in the Geochemical Laboratory of the Geological Survey of Sweden. Many of the main element analyses were made in the State Raw Materials Laboratory, Trondheim, Norway. C and H were determined on the Sample from station S–37 by Mrs. I. Ortman of the Chemical Laboratory of the Geological Survey of Sweden, and N, F and S were determined on the same sample by the A.B. Kemibyrå, Stockholm. Th and U were determined by the laboratory of the A.B. Atomenergi, Stockholm, by co-operation with Ing. R. Rynninger. Many of the U determinations were carried out by both colorimetry and fluorimetry, with good agreement.

Effort was made in the case of all non-standard quantitative techniques except Sn to check both precision and accuracy of the methods.*

The rounding of results in Tables 1 and 4 indicates the approximate reproducibility of the determinations. In some cases the analytical reproducibility might have warranted an additional decimal, but sampling variations and other considerations suggest that no real gain would be effected by such additions.

Qualitative X-ray examinations were made by means of a Philips powder diffractometer and by oriented and unoriented powder photographs, all with CuK_α radiation. Fil. Lic. B. Aronsson of the Chemical Institute, Uppsala, kindly undertook preparation of additional powder photographs of several sediments by means of CrK_α radiation.

Redox potential and pH were determined by methods similar to those of Emery and Rittenberg (1952), with the exception that pH was always determined on undiluted sediment. The main purpose of the *E*H measurements was as an indicator of the degree of stagnation, and the values are not to be regarded as physicochemically exact measurements. However, these values may well correspond to an upper maximum of the "true" *E*H *in situ*, and accordingly have some value in delimiting stability fields for certain minerals and chemical combinations.

Results

Environmental relationships

The sediments of the central Baltic show a distinct character unlike the sediments of the Cattegat, Skagerack and North Sea or other common nearshore

* A final check on the accuracy of the Zn and Pb determinations has not yet been made, but preliminary studies indicate that systematic errors are probably not present.

types. Notable features are the presence of eroded peneglacial and proglacial sediments in zones of scour and fine-grained, stagnant sediments in the basins.

One of the most significant features of the Baltic Sea is its salinity stratification, which may be seen in Fig. 2 (profile *A–A'*, Fig. 1). The salinity stratification and its concomitant density stratification are relatively permanent features in the Baltic. They prevent aeration of the deeper areas by thermal mixing and give rise

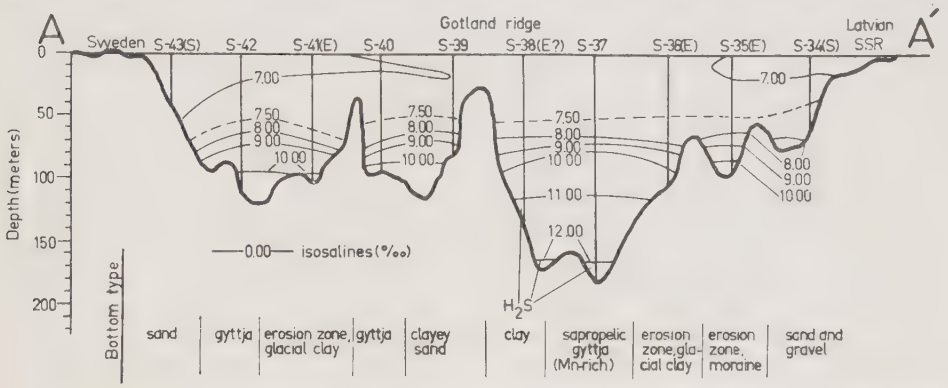

Fig. 2. Salinity and sediment distribution along profile *A–A'*. Sediment types refer only to sediment at station indicated.

to the permanent oxygen deficits found in many of the deeps. Fig. 3 shows the typical distribution with depth of pH, *E*H, salinity and O_2 in the Gotland Deep, station S–33. No particular significance is attributed to *E*H values above about 0·30 to 0·35 V, except that they indicate oxygenation of the water. However, as may be seen, the redox potential does show a relationship to the oxygen content down to the region where H_2S is encountered. According to S. Fonselius (personal communication) the H_2S level in the Gotland Deep was unusually low in 1959. In the H_2S zone there is a sharp drop in *E*H and a rise in pH. The rise is considered to be more associated with the bacterial reduction of sulphate and consequent liberation of free base than with ammonia production, since hydrographic investigations by the Finnish vessel, *Aranda* have shown, if anything, a decrease in ammonia content of the deepest water in the Landsort and Norrköping Deeps (Hela and Koroleff, 1958), and there are as yet no data indicating that the situation is different in the Gotland Deep. Another possible contributor to the increased pH may be the production of bicarbonate due to interaction of carbonic acid with carbonate detritus.

If we consider a profile such as Fig. 4 (*B–B'* in Fig. 1) we find that as soon as the waters are deep or quiet enough to permit fine sediment to be deposited, stagnation has also set in, generally accompanied by H_2S formation. As a result, the central Baltic sediments show an unusually short transition from fairly coarse, oxygenated sediment to fine, stagnant sediments. Starting from the coast of Öland (Sweden) in Fig. 4 we find coarse sand and gravel with high *E*H values and mildly alkaline pH in both sediment and overlying water. The clayey sand shows a decrease in *E*H in the sediment and a slight decrease in the overlying water. Proceeding farther into the basin a gyttja (green-grey, organic muck) characterized

by the presence of H_2S is found, followed by another gyttja. While the EH in the gyttjas is sharply lower, the EH values in the overlying water indicate the presence of considerable dissolved oxygen. Full aeration is again found around the erosion zones near the Gotland ridge. On passing into the easternmost basin (Gotland Deep) we find more strongly reducing conditions, as indicated by EH, and the

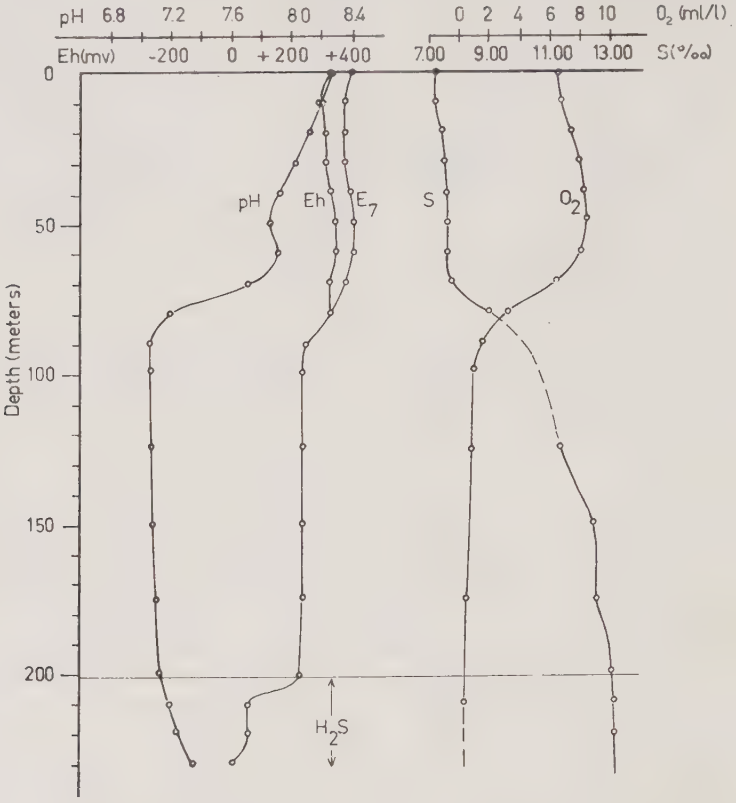

Fig. 3. Distribution of pH, EH, salinity and dissolved oxygen with depth in the Gotland Deep. Location 57° 21′ N, 19° 57′ E. Station 33(F–81).

formation of black sapropels. Proceeding further eastward the black oozes grade into a gyttja characterized by higher redox potential, and finally into an oxygenated, slightly calcareous sand as the coast of Latvia is approached.

A significant difference may be pointed out between the environmental conditions of the sapropels and the gyttjas. In the former both sediment and the overlying water are stagnant and characterized by the presence of H_2S, while in the case of the gyttjas the sediment is reducing, with or without the presence of H_2S, but the overlying water contains considerable dissolved oxygen.

The pH in the two basins illustrated also shows interesting relationships. In the westernmost basin the pH in the bottom water is higher than in the sediment, while in the eastern basin the opposite relation holds, and on the whole both sediment and overlying water are more alkaline than the former basin. This condition seems to be to a considerable extent occasioned by the source material

of the sediments. Ordovician limestones are exposed on Öland, but in the area of erosion and scouring along the bottoms Cambro–Ordovician shales and sandstones and pre-Cambrian metamorphics appear to dominate. Glacial and proglacial sediments exposed by erosion both to the north and south of profile *B–B′* have higher carbonate contents, but the carbonate from this source appears to have been largely dissipated in the course of reworking and redeposition of the sediments.

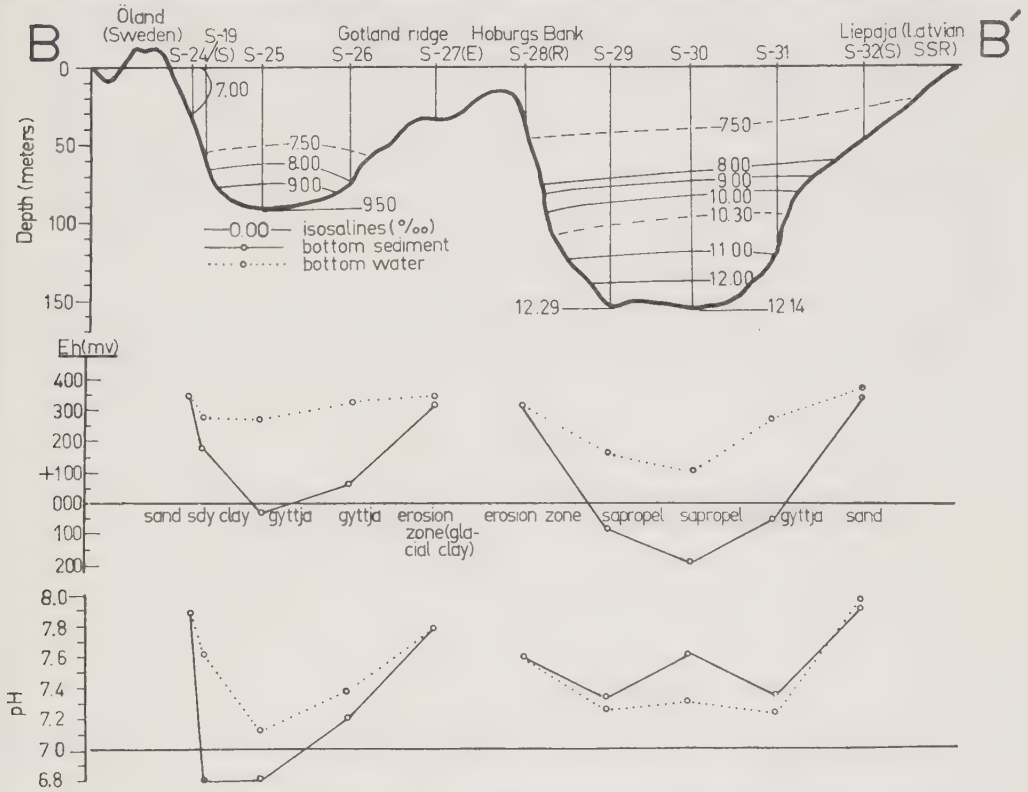

Fig. 4. Salinity, sediment type, *E*H and pH distribution along profile *B–B′*. Sediment types refer only to sediment at station indicated.

Where carbonate detritus is absent the CO_2 formed through decomposition of organic material will tend to form carbonic acid directly, resulting in a lowering of the pH. Since production of CO_2 is greatest in the upper sediment layers where organic matter is concentrated and where bacteria reach their greatest abundance, the pH tends to be lower in the sediment than in the overlying water. Such ammonia and organic acids which may be produced simultaneously appear to be subordinate in their effect on pH because of the overwhelming preponderance of CO_2 production. In the Gotland Deep, however, the source materials contain abundant carbonate, and the basement rock on which the basal glacial sediments rest are themselves believed to be Silurian carbonates and marls. Where the sediments contain appreciable carbonates the CO_2 from decomposing organic matter will first attack the carbonate with the formation of bicarbonates, which in turn will tend to raise the pH. The pH may be expected to be influenced not

only by the bicarbonate ion, but also by the direct presence of finely divided carbonate material, and by the liberation of free base through sulphate reduction, which is undoubtedly intense in this basin, as testified by the low redox potentials.

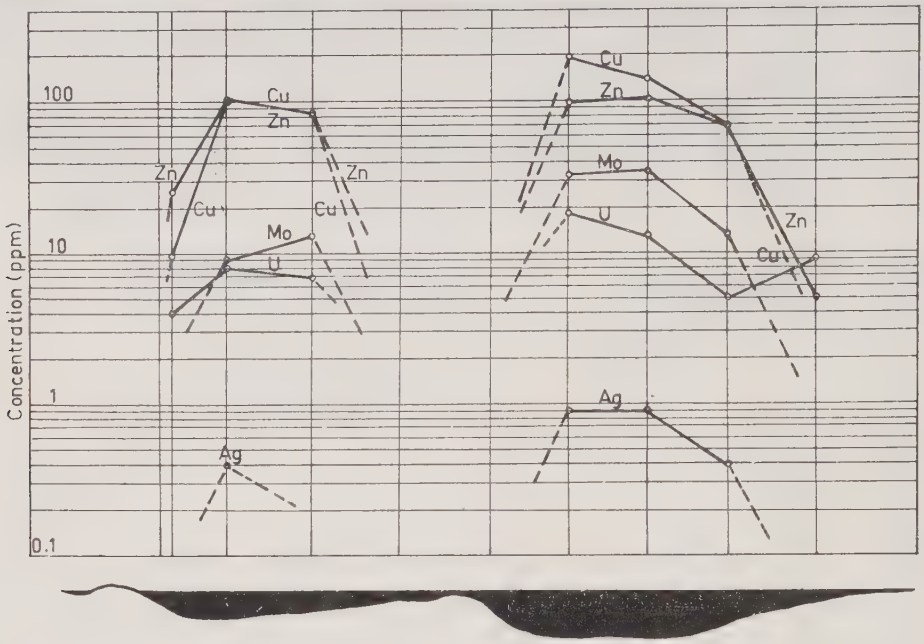

Fig. 5. Distribution of Cu, Zn, Mo, U and Ag along profile *B–B′*. The dashed lines show the general expected range of concentration to stations where no data points are shown. The ranges are partly inferred from "less than" determinations on sediments from such stations. Mo is irregularly distributed in the sediment at station S–29 (see Fig. 4) and values up to 80 g/ton were found.

The above explanation for the pH distribution is confirmed by CO_2 analyses in the sediments of the two basins. It was found, for example, that where carbonate (expressed as per cent CO_2) was less than 0·10 the pH was generally about 7·0 or lower.

Variations in Heavy Metal Concentration

Fig. 5 shows the concentration of a number of key heavy metals along the same profile, *B–B′*, discussed above. These metals show a general sharp increase in going from sands and clayey sands to gyttjas and an even greater enrichment in the sapropels. This increase was particularly evident for Cu, Ag, U and Mo. The unusually large uranium concentration in the sand at position S–32, 9 p.p.m., suggests a local concentration of uranium-enriched detrital material at this position on the Latvian shelf. The relatively large uranium concentration in the clayey sand at S–19 is attributable to Cambro–Ordovician alum shale detritus, which was found present in the sediment. These shales are well known for their enrichment in uranium.

The difference in heavy metal concentrations at the two stations, S–29 and S–30 points up some interesting features. Station 30 not only had a lower *E*H than S–29, both in sediment and bottom water, but it also had about half again as much organic material, as well as a geographical position closer to the centre of

the Gotland Deep. In spite of these factors S–29 showed higher Cu and U values than S–30, and both stations showed higher values than S–33 in the deepest part of the Gotland Deep. Close spacing of sediment samples in an area not indicated in Fig. 1 confirmed the fact that heavy metals in general are not concentrated in the central, most stagnant parts of the basins, but around the peripheries, in the transition zone to stagnant conditions.* In such areas contents as high as 250 p.p.m. Cu, 250 p.p.m. Zn, 32 p.p.m. U, 80 p.p.m. Mo and 1·6 p.p.m. Ag were found. Sn and Pb data are not yet complete but indicate the same phenomenon. Mo has an additional strong tendency to follow iron sulphides, while another element often placed in the chalcophilic group, gallium, shows no observable tendency to be enriched in the transition zone.

The highest uranium concentration found in the Baltic was 130 p.p.m. in a black, homogeneous "Ancylus" clay taken from about 250 cm from the top of the core at S–33(F–81). "Ancylus" refers to a stage of the Baltic Sea following the closing of the central Swedish sea channel (ca. 7000 B.C. according to Magnusson *et al.*, 1957) during which the surface water became fresh. The position of the sediment is inferred from lithology and its stratigraphic position in the core sequence, but in the absence of spore and pollen and faunal data the use of the term is only tentative.

It is interesting to note that surficial sediment from the same hydrographic station as above was analysed by Koczy *et al.* (1957) for uranium. These workers found from ca. 4 to 10 p.p.m. uranium in three samples from the upper 26 cm of their sediment core, in rather good agreement with the present result of 6 p.p.m in a sample representing an average of the upper 30 cm.

Distribution of uranium

The findings in the present study are not consistent with the explanation for the distribution of uranium in the Baltic sediments advanced by Koczy *et al.* (1957). In accordance with accepted concepts, these authors ascribed the geochemical behaviour of uranium to the reduction of the easily soluble $U^{(VI)}$ form to the less soluble $U^{(IV)}$ form. They then, however, went on to state:

> Man kann sich den Prozess der Ausfällung so vorstellen, daß das U(VI)-Ion durch organische Stoffe zum U(IV)-Ion reduziert und an organischem Detritus adsorbiert wird, wobei kolloidale Lösungen resultieren. Dadurch wird das Uran dem Oberflächenwasser entzogen, sinkt langsam ab und reichert sich im Tiefenwasser an, wo es, da Sauerstoffmangel herrscht, nicht wieder in Lösung gebracht werden kann.

As evidence for this process is cited that surface waters showed lower uranium content than waters in the Gotland and Landsort Deeps.

If adsorption of uranium on organic material at the surface and the subsequent sinking of this material were responsible for the enrichment of uranium in the sediment one would expect uranium to be most concentrated in the centres of the basins, where organic matter reaches its greatest enrichment and where the degree of stagnation is also usually the greatest. The areal distribution of the above author's data was not sufficient to test this possibility. According to the present data,

* Borchert (1959) has reported that maximum enrichment of zinc in the Mansfelder Kupferschiefer occurs in the inferred transition from gyttja to sapropel.

however, neither uranium nor such metals as Cu, Pb, Zn, Ag or Sn are enriched in such a manner, and in fact, maximum enrichment of all these metals was found at positions near the periphery of the stagnant zones, as in the schematic diagram, Fig. 6.

Comparing the average uranium content of the upper sediment layers in the Gotland deep obtained by both Koczy *et al.* and the present investigation, 6–7

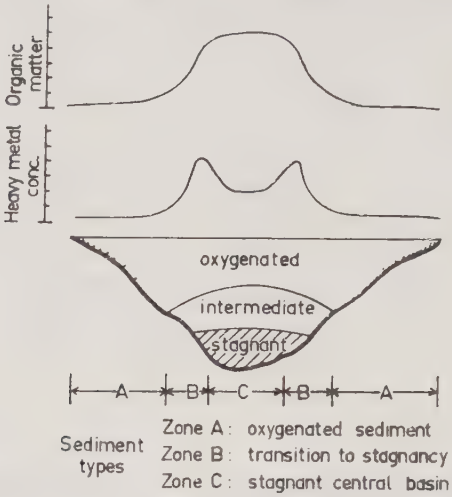

Fig. 6. Schematic distribution of heavy metals across stagnant basins in the central Baltic. The environmental designation of sediment types refers to the environment of the sediment during and just after its deposition. It does not refer to such conditions which may arise after burial.

p.p.m., with the equivalent grain size fraction from organic-poor near-shore sediments, estimated at at least 5 p.p.m., we find that the rain of organic debris from the surficial waters can have contributed a maximum of 2 p.p.m. to the uranium concentration of the deep basin sediment, and it is very probable that the contribution is less.

One might also comment on the higher uranium concentrations in the deep waters than in the surface waters of the Gotland Deep, as found by Koczy *et al.* Even assuming that the higher uranium concentrations are due to insoluble complexes of the type envisaged by the cited authors, there is no proof to show that such matter is not carried in from the basin peripheries instead of coming from above. Unfortunately, the authors reported their water analyses carried out on unfiltered samples, and it is therefore not known to what extent suspended matter contributed to the recorded concentrations.*

It is thus evident that the hypothesis of removal of uranium from surficial waters and subsequent sinking can hardly explain the concentrations of 18–32 p.p.m. and possibly higher which may be found in peripheral stagnant areas of the Baltic.

* Koliadin *et al.* (1960) have analysed samples from a 2000 m column of water from the central Black Sea and reported that throughout the column uranium was virtually entirely in soluble, presumably $U^{(VI)}$ form.

Swanson (1960), after a comprehensive survey of available data on uranium and organic matter in black shales, linked the enrichment of uranium to land-derived humic material. However, in view of the uranium distribution pattern described, we must also limit this mechanism to a subsidiary role in the case of central Baltic sediments. It is not claimed that the conditions found in the Baltic Sea invalidate the conclusions of Swanson and other authors on the origin of many black shales. However, it is felt that they do point out the need for caution in applying a generalized theory of origin to all uranium-enriched black sediments.

In the writer's opinion, Swanson's summary indicates that the large amount of study which has been given to fossil black sediments has yielded disappointingly incomplete understanding of the processes of uranium enrichment in them. It is suggested that investigation of the environment, chemistry and mineralogy of black sediments now forming in various parts of the world will provide a more direct and conclusive approach to the elucidation of these questions.

Enrichment of trace elements

The suggestion is put forward that enrichment of trace elements may be considered as a function of three factors:

(1) Supply.
(2) Removal (concentration) mechanism.
(3) Dilution.

These factors are believed to form a useful frame of reference for investigations of the origin of trace element concentrations in sediments. We wish now to consider how these factors contribute to the uranium present in the three zones in Fig. 6.

In zone *A* (oxidized sediment) the uranium concentration is primarily governed by the supply, i.e. the original uranium concentration of the finest particulate matter, modified by dilution with low-uranium sand and silt. Enrichment in sand such as encountered on the Latvian shelf (S–32) is for the moment disregarded.

In zone *B* all three factors are effective. Dilution by sandy detritus is reduced in accordance with the marked decrease in mean grain size, and organic matter becomes an important constituent of the sediment, and possibly a source of uranium. However, it is evident that neither inorganic nor organic particulate matter is able to account for more than a fraction of the total uranium content in the zones of maximum enrichment, and a powerful removal mechanism is clearly effective in the stagnant transition zone to extract uranium from the water and deposit it with the sediment. The major element concentrations of the sediment show little change across this transition, with the exception of a general increase in sulphur and organic matter toward the basin deeps. Assuming the redox potential is low enough to permit complete conversion of uranium to the $U^{(IV)}$ form, or that other agents are here effective to promote maximum removal from the water, the chief control of uranium concentration in the sediment in the vicinity of the transition zone becomes the amount of uranium available from the water and the dilution of this uranium by the bulk of the sediment deposited, whether of organic or inorganic origin. Organic matter is necessary in order to help create the physico-chemical conditions (stagnation) under which the removal mechanism may become

effective, but it is clear that the threshhold amounts required for this purpose may vary greatly in different environments.

In zone *C* all three factors will again be operative, but in addition to the more static and sterile character of the lower water masses, such water as passes into the area over the bottom from the peripheries of the basin will be impoverished in heavy metals at the transition zone, and the supply of uranium correspondingly diminished.

The effectiveness of the removal mechanism at the transition zone may be judged by the fact that the uranium concentrations found in the centres of the deeps, 6–7 p.p.m., represent only a slight enrichment over the general median for sediments investigated from Swedish coastal or adjoining waters which were not considered to have been laid down under stagnant conditions. This median, 5–6 p.p.m., is based on data from about seventeen sediment samples. If this median is regarded as typical of central and southern Swedish coastal and offshore sediments, then these sediments are higher in uranium than the world-wide average attributed to recent and fossil sediments by a factor of about 1·5 to 2. Such enrichment might be at least partly explained by the erosion of uranium-rich sediments from the mainland during the previous glacial period and the continuing redeposition of these glacial sediments at the present time.

The deep basin uranium concentrations are also similar to those found by Starik *et al.* (1959) in surficial sediments from the central Black Sea. It would be interesting to see whether enrichment patterns similar to those described here might occur in transition zones in the Black Sea, such as might be present near the inflow channel at the Bosporus.

Manganese–iron concretions

Metal oxide concretions were found resting on a clayey sand at station S–19. A semiquantitative analysis of a number of elements in the outer layer of one of these concretions, as well as a quantitative analysis of the underlying sediment is presented in Table 1. According to discussion with Mr. M. Sippola, the trace values for the nodules presented here are not in discordance with a number of determinations made on similar concretions from the Bothnian Sea by the Finnish Geological survey.

It may be noted that manganese nodules are common in the general Baltic Sea area in nearshore and other aerated areas not subject to excess sedimentation. The appearance of the present nodules is virtually identical to those shown opposite p. 96 in Gripenberg (1934), originating from the Gulf of Finland. The appearance of the nodules is also rather similar to concretions described from a fresh water Nova Scotian lake (Kindle, 1932) in regard to the presence of two discrete types. Kindle found a larger, flattened to discoidal form ranging to ca. 30 mm in diameter and consisting of concentric layers of oxide developed from a pebble as nucleus. A smaller ovoid form had no apparent foreign object as nucleus. Kindle suggested that the latter type had been formed about a broken concretionary fragment and rolled around on the bottom, permitting an even accretion of oxide.

The manner of the present occurrence, however, is different from that of the

lacustrine nodules. KINDLE's specimens were found in shallow water only 2 to 6 ft deep and were obviously affected by the photosynthetic activity of diatoms and other life. One nodule was found growing out from a pebble only in the direction of light, while the shaded side was bare. The present depth of 58 m

Table 1. Analysis of manganese–iron concretions and underlying sediment, station S–19. (Position 56°26′ N, 16° 48′ E; depth 58 m. All concentrations in weight per cent based on oven dried sediment in equilibrium with atmospheric moisture. The sample (sediment) analyzed is probably sandier than the average sediment *in situ*).

Semiquantitative analysis of manganese–iron nodules	Quantitative analysis of sediment*			
	Major elements		Trace elements	
Fe major constituent	SiO_2	80	Sr	0·0100
Mn major constituent	Al_2O_3	8·5	Ba	0·064
Si 0·3–3	MgO	0·99	Rb	0·0055
Al 0·2–2	CaO	0·90	Li	0·0019
Mg 0·1–1	Fe_2O_3(tot.)	2·5	Ni	0·0012
Ca present	MnO(tot.)	0·027	Cr	0·0037
Ti present	TiO_2	0·49	Co	0·0003
P 0·1–1	K_2O	1·7	V	0·0030
B 0·01–0·03	Na_2O	1·7	Ga	0·0006
As 0·01–0·03	CO_2	<0·03	Th	0·0008
Pb 0·01–0·03	H_2O^-	0·41	U	0·0004
Zn 0·01–0·03	Ign. loss (1000°C):	2·7	Zn	0·0032
Ni 0·003–0·01			Cu	0·0010
Cu 0·003–0·01			Pb	<0·0010
Co 0·002–0·006			Sn	<0·0005
V 0·0003–0·001			Mo	<0·0002
Cd 0·0003–0·001			Ag	<0·00003
Sn 0·0001–0·0003				
Be 0·0001–0·0003				
Cr <0·0005				
Ga <0·0005				
Ge <0·0010				
Mo <0·0005				

Bottom sediment type: clayey to silty sand with subangular to subrounded pebbles and manganese–iron concretions lying on surface.
Interstitial water content: 36 per cent bulk weight
Bottom water salinity: 7·80 ‰ (calc. from Knudsen tables based on Cl^-).

* The analyses are uncorrected for the salt content of the interstitial water (36·0 per cent) of the original bulk sediment. Correction for this factor would lower the values for Na and to a lesser extent Mg. Other elements would not be significantly affected.

indicates that photosynthetic raising of pH and other effects must be much smaller, if at all present. Furthermore, the present nodules are associated with brackish waters of 7·8 ‰ salinity.

The underlying clayey sediment showed an *E*H of 0·168 V and a pH of 6·8, while the overlying water had an *E*H of 0·280 V and pH of 7·6. Consideration of the *E*H–pH stability and solubility fields of iron and manganese suggests that the leachable portion of these elements may be stable in soluble divalent form and

that they may tend to migrate to the surface of the sediment. Here the higher *E*H and pH would tend to cause their oxidation to higher valencies and precipitation on suitable nuclei. Kindle showed that the deposition of oxides is a highly selective process, and that once formed, the scavenging (catalytic) properties of the manganese oxide concretions permit their growth even where surrounding pebbles remain uncoated with oxide.

It thus appears likely that the present concretions began under conditions of chemical or biochemical precipitation of manganese oxide, but that once formed, the growth could proceed even in periods when no uncatalysed precipitation of Mn and Fe would occur. It also appears likely that a part of the material for the present concretions came from the underlying sediment. The bottom conditions in this area change considerably with season, and also no doubt show secular changes. Corresponding *E*H–pH changes and metal concentrations in the water might then be expected to exert their influence on the proportion of Fe and Mn deposited on the nodules.

Quantitative chemical studies of such nodules are projected for the near future, but the present semiquantitative analyses serve to illustrate the markedly lower trace element concentrations in these nodules than in Pacific and other deep sea concretions (Clarke, 1924; Goldberg, 1954). The difference is probably related to the much more rapid growth of the present nodules than the deep-sea types. One evidence of the recent character of the present deposit is the presence of broken grains of fresh alum shale (Cambro–Ordovician shales previously mentioned) covered with thin limonitic skins. These euxinic shales weather rapidly in oxidizing environment but the present grains only showed the beginnings of limonitic stains along bedding planes within the grains.

Occurrence of manganese-rich stagnant sediments

One of the unlooked-for features of the present investigation was the finding of extraordinary concentrations of manganese in sediments from two of the central Baltic deeps, stations S–37(F–80) and S–33(F–81). In the former sediment the manganese amounted to 5·2 per cent MnO. Manganese concentrations integrally present in recent sediments, as opposed to surficial crusts or nodules, are known from a number of areas, such as the Atlantic and Pacific Oceans, the Sea of Okhotsk and the Norwegian Sea. In these cases, however, the bulk of the manganese appears to be in the form of higher oxides or hydrated oxides. Ordinary stagnant sediments, on the other hand, are generally characterized by low manganese concentrations, as may be seen in Table 2.

Inasmuch as both the present sediment and the overlying water are stagnant and characterized by free H_2S, stability considerations suggest the presence of manganese oxides or hydrated oxides to be most unlikely. Chemical tests showed that the bulk of the manganese was in acid-soluble form and not in a silicate phase. Manganese sulphide (alabandite) is virtually excluded on solubility grounds and the author is not aware of reports on the occurrence of hauerite (MnS_2) in sediments. The most reasonable compound remaining thus appears to be rhodochrosite or mixed carbonates of Mn, Ca, Fe and Mg. This possibility was reinforced by the high carbonate concentration in sediment S–37, 4·7 per cent CO_2, which is larger

than could be accounted for even if all the calcium (2·2 per cent CaO) were present in carbonate form. Leaching of the washed sediment with dilute acetic acid, a method considered to attack only carbonates (VESTERBERG, cited in GRIPENBERG, 1934), followed by semiquantitative spectrographic examination of the leachate found Mn > Ca > Fe ~ Mg.

Table 2. Distribution of manganese in various sediment types

Material	MnO (wt. %)
Average deep sea clay, carbonate free (TUREKIAN, *et al.* 1961).	0·86
"World" average, clay sediments and shales (WEDEPOHL, 1960)	0·11
25 stagnant bottom sediments from the Stockholm Fjärd (present writer, unpub. data).	0·066
Stagnant medial mucks, Black Sea (OSTROUMOV, 1955)	0·058
Swedish Cambro–Ordovician alum (oil) shales (G. ASSARSSON, pers. comm.; writer, unpub. data)	0·02
Fårö Deep (S–37, F–80)	5·2
Gotland Deep (S–33, F–81)	3·1

The conclusion that manganese was largely in the form of carbonate was further confirmed by X-ray powder and diffractometer analyses. These studies detected no manganese oxides, calcite, aragonite or dolomite, but showed presence of a broadened line ($d \sim 2{\cdot}90$) which would correspond approximately to a solid solution mixed carbonate having the proportions

$$Ca_{30}\,Mn_{70}\,CO_3$$
$$Ca_{32}\,Mn_{60}\,Mg_8\,CO_3, \text{ etc.}$$

according to data of GOLDSMITH and GRAF (1960). Non-manganese-rich sediments from the periphery of the basin with otherwise similar composition did not show this line. The line was sharpened on heating the powder to 220°C, was not altered on leaching with hot water, but disappeared on leaching with 0·2 N HCl.

A calculation based on the excess Ca, Mg, Fe and Mn in this sediment over similar but non-carbonatic stagnant sediments in the area gives the result shown in Table 3.

Thus, calculation of a hypothetical mixed carbonate based on excess cations

Table 3. Composition of a mixed carbonate corresponding to excess cations

	Weight % found in S–37	Excess oxide over "normal" non-carbonatic stagn. sed.	Corresp. CO_2
CaO	2·2	0·9 ± 0·4	0·7 ± 0·3
MgO	2·7	0·5 ± 0·3	0·5 ± 0·3
FeO	6·8	0·5 ± 0·5	0·3 ± 0·3
MnO	5·2	5·1 ± 0·1	3·1 ± 0·1
		total	4·6 ± 1·0
CO_2	4·7	4·7 ± 0·1	4·7 ± 0·1

gives good agreement with carbonate actually found, although the very close correspondence may be accidental. Converting to atomic per cent and leaving out iron would give a carbonate with approximately the following formula: $(Mn_{72}$ Ca_{16} $Mg_{12})CO_3$. Iron is left out since it may tend to preferentially form sulphides or may be in a separate phase (see later). The manganese concentration in the above formula would check well with the X-ray formula if virtually no magnesium were present. The problem is that the X-ray data suggest more calcium and less manganese than chemical calculation permits.

While it has not yet been possible to reconcile the data in a more satisfactory manner than shown above, the evidence indicates that we have, in these sediments, a mixed manganese carbonate of some type. With less assurance one may suggest that the structure corresponds to that of rhodochrosite and that the chief admixture is calcium, with magnesium and iron possibly present. The full analysis is presented in Tables 4 and 5.

The manganese-rich sediments are dark greenish-grey to black when fresh and are highly organic and fine-grained. No discrete minerogene particles were visible under low power binocular microscope. Microscopic observation of the sediment during leaching with dilute HCl, however, showed that the carbonate is unevenly distributed in lumpy, irregular zones from less than 1 mm to several millimetres in diameter. These zones are enriched in manganese, as revealed by qualitative spectrographic examination, and may be responsible for the irregular distribution of carbonate previously noted in central Baltic post-glacial sediments. For example, Gripenberg (1934) found CO_2 concentrations corresponding to 1·68, 1·84, 2·45 and 3·78 per cent "$CaCO_3$" in four samples from F–80, corresponding to the present station S–37.

Debyser (1957) found that formation of siderite spherulites in the deep Baltic sediments was associated with both stagnation and a source of available carbonate. In the absence of the latter no siderite could be observed. In the present sediment from S–37 a weak line corresponding to the main X-ray line of siderite was observed with CrK_α radiation but not with CuK_α. The line was also not visible in non-carbonatic sediments with similar composition (except Mn). If this indication is correct, siderite would appear to form in a separate phase from the manganese–calcium carbonate.

It is interesting to note that already before 1900 Munthe (1894) discussed the anomalous carbonate content of certain Baltic clayey bottom samples taken in the Swedish Hydrographic Expedition of 1877. One such sediment contained 2·56 per cent CO_2, corresponding to 5·8 per cent $CaCO_3$, while the HCl-leachable Ca was equivalent to only 3·05 per cent $CaCO_3$. The unaccounted-for carbonate was recognized as being even greater than this apparent difference, since Munthe was aware of the fact that total HCl leachable Ca was nearly always larger than that attributable to the carbonate phase. Neither Munthe nor Gripenberg in her later investigations determined manganese in the sediments, and Munthe attributed the excess carbonate to $MgCO_3$. In accordance with the evidence cited heretofore, however, it is reasonable to suppose that the excess carbonate was actually due to presence of $MnCO_3$-mixed carbonates.*

* Zen (1959) has identified rhodochrosite in sediments from the Peru-Chile trench.

Summary

(1) Central Baltic sediments show an unusually short basinward transition from coarse, oxygenated sediment to fine, stagnant sediment. This condition

Table 4. Analysis of sediment from S–37(F–80), position 58°02′ N, 20°00′ E

(Concentrations in weight per cent of air dry sediment. "A" values are uncorrected for interstitial water, "B" values are corrected for the assumed composition of interstitial water.)

Major elements			Trace elements		
	A	B		A	B
SiO_2	39	39	F	0·053	0·053
Al_2O_3	14·2	14·2	B	0·0120	0·0115
Fe_2O_3(tot. Fe)	7·7	7·7	Sr	0·0135	0·0130
MnO	5·2	5·2	Ba	0·075	0·075
TiO_2	0·72	0·72	Li	0·0038	0·0038
CaO	2·2	2·2	Rb	0·015	0·015
MgO	2·9	2·7	Ni	0·0043	0·0043
Na_2O	1·6	0·3(?)	Co	0·0022	0·0022
K_2O	4·4	4·3	Cr	0·0090	0·0090
C(org.)	4·6	4·6	V	0·0130	0·0130
H(550°C)	1·05	1·05	Mo	0·0035	0·0035
N	0·57	0·57	Cu	0·0078	0·0078
P	0·10	0·10	Zn	0·0110	0·0110
S(tot.)	2·8	2·8	Pb	0·0025	0·0025
CO_2	4·7	4·7	Sn	0·0008	0·0008
Cl^-(calc.)	1·9		Ag	<0·0001	<0·0001
$H_2O^-(P_2O_5)$	2·2		Ga	0·0030	0·0030
Ig. loss (550°C)	13·1		U	0·0007	0·0007
Ig. loss (1000°C)*	18·0		Th	0·0011	0·0011

Bottom water salinity (‰)	12·03
Bottom water O_2 (ml/l.)	0
Bottom water H_2S	present
Bottom water temp. (°C)	5·18
Bottom water density (σ^t)	9·56
Bottom water pH	7·25
Bottom water *Eh* (V)	0·045
Bottom sediment interstit. water (% bulk wt.)	71·0
Bottom sediment sampling depth (m)	188
Bottom sediment H_2S	present
Bottom sediment pH	7·4
Bottom sediment *Eh* (V)	−0·130
Bottom sediment type: foul-smelling greenish-black muck with indistinct organic stratification	

* Ignition loss at 1000°C is referred to the dry sediment.

is due to the salinity stratification of the Baltic Sea and the permanent oxygen deficits found in the deeper layers. Sapropelic sediments with high organic content may be found in the deeps, where overlying water is characterized by very

low or nil oxygen concentration. Gyttjas (grey-green organic mucks) are formed in quiet areas where some oxygen renewal in the water takes place. Hydrogen ion activity around pH 7 or lower and lower pH in the sediment than in the overlying water is characteristic of low-carbonate sediments, while higher pH values are found in sediments containing appreciable carbonate content.

(2) Heavy trace metals such as Cu, Ag and U, as well as Mo tend to be enriched in the sapropels, but with the possible exception of Mo, maximum enrichment occurs not in the centres but at the peripheries of the stagnant basins. Mo appears to follow iron sulphides, presumably due to co-precipitation phenomena. Maximum

Table 5. X-ray examination of sediment from station S–37
(The intensity indications cannot be used for more than qualitative indications of the mineral species present because of matrix, grain size and other effects.)

Minerals detected	Intensity	Minerals sought but not detected
quartz	very strong	kaolinite
K-feldspars	strong	marcasite
montmorillonoids	strong (v. broad)	pyrrhotite
halite*	strong–medium	calcite
well-crystallized micas	strong–medium	aragonite
calcic rhodochrosite (?)	strong–medium	dolomite
undifferentiated (non-K) feldspars	medium	manganese oxides (pyrolusite, manganite, etc.)
chlorite	medium	alabandite (MnS)
illite	medium	hauerite (MnS_2)
pyrite	weak	rhodochrosite (pure)
siderite	medium-weak (CrK_α radiation only)	"melnikovite"†

* Due to interstitial water.
† *sensu* Lepp (1957) and Korolev (1958); however, any reactive sulphides would probably have been destroyed in the drying process.

uranium content found in the Baltic was 130 g/ton. The data are not consistent with the hypothesis, advanced by Koczy *et al.* (1957) that uranium forms insoluble complexes with organic matter in the surface waters and then sinks to the bottom. Rather, direct precipitation, co-precipitation or adsorption from water is indicated.

(3) Analyses of manganese–iron concretions and the underlying sediment from one station are presented. The concretions are similar to previously described nodules from the Gulf of Finland but differ from deep sea nodules in their lower trace element content. The *E*H–pH conditions are such that leachable Mn and Fe would appear to be soluble in the interstitial water of the sediment, but not in the overlying water, suggesting that the sediment is a source of metal for the nodules.

(4) Manganese-rich stagnant sediments were found in two of the central Baltic deeps with concentrations as high as 5·2 per cent MnO. Chemical, X-ray and lithologic evidence suggest that a mixed manganese carbonate is responsible for the enrichment.

Acknowledgments—The bulk of the work has been carried out at the Geochemical Laboratory of the Geological Survey of Sweden, and a debt is acknowledged to the former and present

directors of the Survey, Dr. N. H. Magnusson and Mr. K. A. Lindbergson, and to the head of the Geochemical Laboratory, Dr. S. Landergren for making available research facilities to the writer. The assistance and advice of Fil. Lic. K. Fredriksson, Mrs. A. Byström-Asklund and Dr. G. Assarsson of the Geochemical and Chemical Laboratories of the Survey are acknowledged with pleasure, as is the helpfulness of Miss B. Rajandi and other members of the staff of the above laboratories.

The writer is indebted to Professor B. Kullenberg of the Göteborg Oceanographic Institute for permission to join an expedition for the purpose of taking bottom samples and for permission to utilize hydrographic data from the cruise. Thanks are also extended to Fil. Lic. A. Svansson for his cooperation. Special obligation is acknowledged to Ing. R. Rynninger and the laboratory of the A.B. Atomenergi, Stockholm for the careful determinations of uranium and thorium in the sediments. Fil. Lic. B. Aronsson of the Chemical Institute, Uppsala University, carried out several X-ray determinations. Permission was kindly given by Ing. A. Kvalheim, Director of the State Raw Materials Laboratory, Trondheim Norway, for the writer to carry out a large number of major element analyses on the ARL quantometer at the Laboratory. The helpfulness of Ing. Kvalheim and his staff is gratefully acknowledged. Useful conversations were held with Professor F. Wickman, Dr. J. Eklund, Fil. Lic. B. Dahlman, Fil. Lic. A. Jerbo, Ing. M. Sippola and Dr. H. Ignatius. Mrs. L. Bjugren of the Geological Survey of Sweden assisted the writer with literature references. Financial assistance has been granted toward the defraying of the costs of the research by the Mathematics–Natural Science Faculty of the University of Stockholm and the Swedish Royal Academy of Science.

Finally, the present work would have been impossible without the constant helpfulness of Dr. S. Landergren and Professor I. Hessland, Chairman of the Geological Institute, University of Stockholm. To these, his mentors, the writer should like to express his sincerest gratitude.

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Niobium content of soils from West Africa*

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(*Received* 16 *December* 1960)

Abstract—Analysis of twenty lateritic soil samples from West Africa has shown them to contain an average 24 p.p.m. of niobium; four similar samples taken from within a few miles from a niobium deposit contain from 79 to 87 p.p.m. niobium. It has been shown that as the aluminum content of the soils increases, the following depletion sequence is obtained:

$$Si > Nb > Al = Fe$$

The data indicate that, in general, high enrichments of niobium are not to be expected in lateritic soils.

Introduction

Niobium and tantalum are unique among the elements in that almost all their compounds are insoluble in acid and alkaline media. In the absence of complexing agents, the known soluble compounds of niobium require high concentration of acid or alkali for their formation and stabilization. Because of the insolubility of niobic acid, it was felt that the element might be concentrated in lateritic soils depleted in silica and alkalies.

Although there are few published analyses for niobium in soils, data are available for bauxites. Fleischer *et al.* (1952) found an average of 450 p.p.m. of niobium in forty-six samples of bauxite developed on nepheline syenite in Arkansas; Pearson (1955) reported less than 100 p.p.m. in thirty-seven samples of bauxite derived from gneiss in the Gold Coast, and 500 p.p.m. in laterite derived from alkalic rocks in Nyasaland. Rankama (1948) reported 28 p.p.m. niobium in a laterite from Funchal, Madeira. Burstall and Williams (1952) and Mercer and Williams (1952) found a significantly higher concentration of niobium (13,300 p.p.m.) in a soil from Sukulu, Uganda. This soil, however, contained pyrochlore and cannot be considered to be representative of most soils.

Samples

Samples from West Africa were chosen for study because the area represents a well known region of particularly extensive distribution of lateritic soil. The soil samples used in this work had been collected by Dr. L. T. Alexander of the U.S. Department of agriculture in 1951 during OEEC Technical Mission 47 expedition to West Africa to study laterites (Alexander *et al.*, 1956). The samples were collected in Sierra Leone, Ivory Coast, French Guinea, Dahomey, Nigeria, Gold Coast and the Belgian Congo. Of the many specimens made available, twenty-four were large enough and properly distributed laterally and vertically to warrant use in this study These samples are listed below along with pedological data taken

* Publication authorized by the Director, U.S. Geological Survey.

from Dr. Alexander's log or communicated by him. Unfortunately, no samples of bedrock were available.

French Guinea

No. GF-7-1 (Agriculture 51929). Sample taken 17 April, 1951, from a terrace of the Tinkisso River 18 km north east of Dabola. Structureless sandy loam from surface to depth of 25 cm.

No. GF-7-3 (Agriculture 51931). Same source as GF-7-1. Mottled light clay loam taken 55 cm below surface.

No. GF-8-1 (Agriculture 51932). Sampled on 17 April, 1951, during trip from Kouroussa to the crossing of the Niger River. Profile sample taken 11 km before reaching Kankan. Sample from surface to depth of 15 cm of granular gravelly clay loam containing many roots. The soil at this location is derived from granite.

No. GF-8-3 (Agriculture 51934). Same data as for GF-8-1. Taken from depth of 40–75 cm.

No. GF-8-4 (Agriculture 51935). Same source as GF-8-1, and taken from depth of 75–80 cm. Sample contains red mottled granitic fragments and pistolites from a former lateritic crust.

Sierra Leone

No. SL-1-1 (Agriculture 51907). Sampled 2 April, 1951 in no. 10 pit 70 ft into forest from edge of open area near York. Granular, gravelly, gritty, heavy loam from surface to depth of 10 cm. This soil horizon may not be a completely pedogenic product, but may have some overwash; it is underlain by norite at an unknown depth.

No. SL-1-5 (Agriculture 51911). Same data as for SL-1-1. Softer mottled material from depth of 370 to 420 cm.

No. SL-2-1 (Agriculture 51912). Sampled 2 April, 1951, 110 ft from the SL-1 profile. Gravelly, gritty, sandy loam with many roots from surface to depth of 9 cm. Underlain by norite.

Ivory Coast

No. CI-5-1 (Agriculture 51948). Sampled 3 May, 1951, north west of Bondoukou. Clay loam with ferruginous gravel and some well rounded quartz gravel. Soil, derived from alluvial material, sampled from surface to depth of 20 cm.

No. CI-5-3 (Agriculture 51950). Same data as for CI-5-1. Sampled at depth of from 40 to 68 cm.

No. CI-5-5 (Agriculture 51952). Same data as for CI-5-1. Light-coloured areas with some quartz gravel but with no concretions. Sample from 105-cm depth.

No. CI-6-1 (Agriculture 51953). Sampled 3 May, 1951, 110 m east and 4 m higher in elevation than CI-5 profile. Previously cultivated ground. Heavy silty clay loam from surface to depth of 20 cm. Soil developed on alluvial material.

No. CI-6-3 (Agriculture 51955). Same as for CI-6-1. Silty clay from depth of from 38 to 70 cm.

No. CI-6-5 (Agriculture 51957). Same as for CI-6-1. Gravelly, silty clay at 110–130 cm depth.

Gold Coast

No. GC-1-1 (Agriculture 51961). Sampled 11 May, 1951, 53.5 miles west of Tamale on road to Damongo. Underlain by schist. The fine sandy loam was sampled from the surface to 10 cm in depth. May have been winnowed by wind action.

No. GC-1-3 (Agriculture 51963). Same site as GC-1-1. Ferruginous gravel, quartz gravel, and schist fragments sampled at depth of from 30 to 80 cm.

Dahomey

No. D-1-1 (Agriculture 51966). Sample taken 19 May, 1951, at edge of town of Djougou at depth of approximately 125 cm. A residual soil underlain by granite.

No. D-2-1 (Agriculture 51968). Sample taken 19 May, 1951, 2 km south of Tchaourou. Sandy loam (0–18 cm) underlain by gneiss having insufficient iron to form a lateritic crust.

Nigeria

No. N-1-2 (Agriculture 51972). Sampled 28 May, 1951, south of Samaru Station. An old peneplain laterite underlain by a coarse-grained granite. Soft laterite sampled 90 cm below the surface.

No. N-4-1 (Agriculture 51977). Sample taken 30 May, 1951, at roadside near Hoss, a mining district. Granular clay loam derived from basalt. Sample from surface to depth of 25 cm.

No. N-4-2 (Agriculture 51978). Same data as for N-4-1. Blocky clay loam at from 25 to 55 cm horizon.

No. N-4-3 (Agriculture 51979). Same data as for N-4-1. Structured clay from 55 to 79 cm deep.

No. N-4-4 (Agriculture 51980). Same data as for N-4-1. Taken from 79 to 100 cm below surface.

Belgian Congo

No. CB-2-3 (Agriculture 51993). Sampled 23 June, 1951 at Keyberg near Elizabethville. The soil is a residuum from a schist or a shale, and is composed of a clay matrix in which some segregation of iron has taken place. Sample was taken at depth of 120 cm.

Analytical Methods

Chemical analyses of the samples were conducted by the U.S. Geological Survey under the direction of W. W. Brannock using methods similar to those previously described (Shapiro and Brannock, 1956). Niobium was determined using the technique developed by Grimaldi (1960). Analytical data are shown in Table 1.

Niobium Content of Soils

The niobium contents of the lateritic soils ranged from 10 to 87 p.p.m. (Table 1). The lowest value (10 p.p.m.) was found in the upper 10 cm of a soil (GC-1-1) underlain by a schist and containing 92.3 per cent silica; the higest value was for a Nigerian soil derived from basalt but close to a tin-mining district and within a few

Table 1. Analyses of soil samples

Location	Sample	No.	Depth (cm)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3* (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	H_2O (%)	TiO_2 (%)	CO_2 (%)	Nb (p.p.m.)
French Guinea	A	GF–7–1	0–25	82·1	8·9	0·81	0·04	0·10	0·32	5·1	2·0	0·66	<0·1	17·9
	B	GF–7–3	55	82·6	9·0	1·6	0·04	0·05	0·22	3·0	2·7	0·62	<0·1	22·4
French Guinea	C	GF–8–1	0–15	61·5	15·4	10·1	0·14	0·10	0·06	0·37	8·7	1·3	<0·1	28·4
	D	GF–8–3	40–75	47·2	26·6	11·2	0·15	0·00	0·05	0·51	13·0	1·3	<0·1	33·5
	E	GF–8–4	75–80	36·2	33·6	14·4	—	—	—	—	14·6	1·0	—	34·0
Sierre Leone	F	SL–1–1	0–10	40·8	22·6	10·6	—	—	—	—	13·9	5·1	—	29·0
	G	SL–1–5	370–420	11·6	41·2	22·8	—	—	—	—	22·1	2·2	—	17·0
	H	SL–2–1†	0–9	36·6	22·4	13·7	0·23	0·03	0·08	0·22	15·7	3·5	<0·1	28·8
Ivory Coast	I	CI–5–1	0–20	42·8	23·4	18·4	0·11	0·05	0·04	0·12	13·2	1·8	<0·1	25·4
	J	CI–5–3	40–68	46·5	23·6	16·2	—	—	—	—	11·7	2·0	—	25
	K	CI–5–5	105	46·6	23·8	16·6	—	—	—	—	11·3	2·0	—	25
Ivory Coast	L	CI–6–1	0–20	46·7	19·5	17·7	—	—	—	—	11·1	1·8	—	27
	M	CI–6–3	38–70	44·6	25·0	16·0	—	—	—	—	12·6	1·5	—	26
	N	CI–6–5	110–130	43·1	24·2	19·5	—	—	—	—	11·8	1·5	—	25
Gold Coast	O	GC–1–1	0–10	92·3	2·0	1·5	0·10	0·09	0·04	0·23	2·1	0·46	<0·1	10·3
	P	GC–1–3	30–80	63·6	8·4	21·9	0·17	0·09	0·08	0·50	5·5	0·68	<0·1	15·3
Dahomey	Q	D–1–1	120	40·7	25·7	21·2	—	—	—	—	11·5	1·3	—	16
	R	D–2–1	0–18	85·3	5·4	2·8	0·14	0·12	0·06	0·64	3·0	1·3	<0·1	26·6
Nigeria	S	N–1–2	90	55·7	22·1	10·6	0·02	0·00	0·04	0·25	10·5	0·90	<0·1	31·8
Nigeria	T	N–4–1	0–25	33·7	27·4	17·8	0·30	0·04	0·06	0·20	16·0	3·5	<0·1	80·6
	U	N–4–2	25–55	33·9	28·3	17·8	—	—	—	—	15·2	3·5	—	80
	V	N–4–3	55–79	34·4	28·5	17·8	—	—	—	—	15·1	3·5	—	79
	W	N–4–4	79–100	31·0	29·0	19·5	—	—	—	—	15·8	3·7	—	87
Belgian Congo	X	CB–2–3	120	54·6	20·6	11·8	0·63	0·06	0·08	2·4	8·4	1·1	<0·1	21

* Total Fe as Fe_2O_3.
† Sample contains much organic matter.

miles from a niobium deposit. There are but slight differences in niobium content with depth, with the average for all samples being 34 p.p.m. If the values for the Nigerian samples (nos. N-4-1 to N-4-4, Table 1) are eliminated as being non-representative, the average becomes 24 p.p.m. This compares with the average value of about 21 p.p.m. for niobium in granites, about 14 p.p.m. for niobium in basic rocks, 24 p.p.m. for niobium in igneous rocks in general (Rankama, 1948), and 20 p.p.m. for niobium in the lithosphere (Swaine, 1955). No enrichment of niobium in lateritic soils above the crustal average is indicated.

Relationship of Niobium to Major Elements of the Soils

The following weight ratios were calculated in an attempt to detect geochemical relationships between niobium and major elements of the soils: SiO_2/Al_2O_3, Fe_2O_3/Al_2O_3, Nb/Al_2O_3, and SiO_2/Nb. These ratios are plotted (Figs. 1 to 4) against per cent Al_2O_3. Per cent SiO_2 would have served equally well for comparison inasmuch as there is an inverse linear relationship between per cent SiO_2 and per cent Al_2O_3 for the twenty-four soil samples analysed.

As shown in Fig. 1, the SiO_2/Al_2O_3 ratios for the samples, when plotted against Al_2O_3 contents, all fall on a smooth curve. This is not surprising inasmuch as the SiO_2/Al_2O_3 ratios of most rocks that may have given rise to the soils also fall on or near this curve. The composition of an average granite (75 per cent SiO_2, 13·5 per cent Al_2O_3) and of an average basalt (52 per cent SiO_2, 15 per cent Al_2O_3) are plotted on Fig. 1 as examples. The general nature of this trend is, moreover, demonstrated by the fact that SiO_2/Al_2O_3 ratios for soils from humid temperate regions may also fall on the curve of Fig. 1 (Lawton, 1955).

A similar plot of per cent Fe_2O_3/per cent Al_2O_3 against per cent Al_2O_3 (Fig. 2) shows that the Fe_2O_3/Al_2O_3 ratio does not vary appreciably with the Al_2O_3 content of the soils. Although the gross constancy is clear, the scatter of points in Fig. 2 may reflect the range of iron contents of source materials from which this suite of soil samples has developed; in this case, an average granite may have about 1·3 per cent Fe_2O_3, whereas an average basalt may have 10 per cent Fe_2O_3. Moreover, local secondary processes imposed upon the soils may tend to differentiate iron with respect to aluminium through movement of iron in its Fe^{2+} state (Eh factors) or precipitation of iron in its Fe^{3+} state (pH factors).

The ratio of niobium to aluminium falls as the aluminium contents of the soils rise (Fig. 3). Only four of the points of Fig. 3 diverge appreciably from the curve, and these points are all for Nigerian soil samples. As has already been noted, these samples were taken close to a niobium deposit and have unusually high niobium contents for soils.

A curve similar to that of Fig. 1 or 3 is again obtained when the SiO_2/Nb ratio is plotted against the Al_2O_3 content of each soil (Fig. 4). Attempts to correlate niobium with titanium have not been sufficiently conclusive.

Discussion

Comparison of Figs. 1 to 4 permits a number of conclusions to be drawn with respect to the interrelationships among Si, Al, Fe and Nb in these lateritic soils. As Al_2O_3 increases, the SiO_2/Al_2O_3 ratio decreases (Fig. 1); the Fe_2O_3/Al_2O_3 ratio

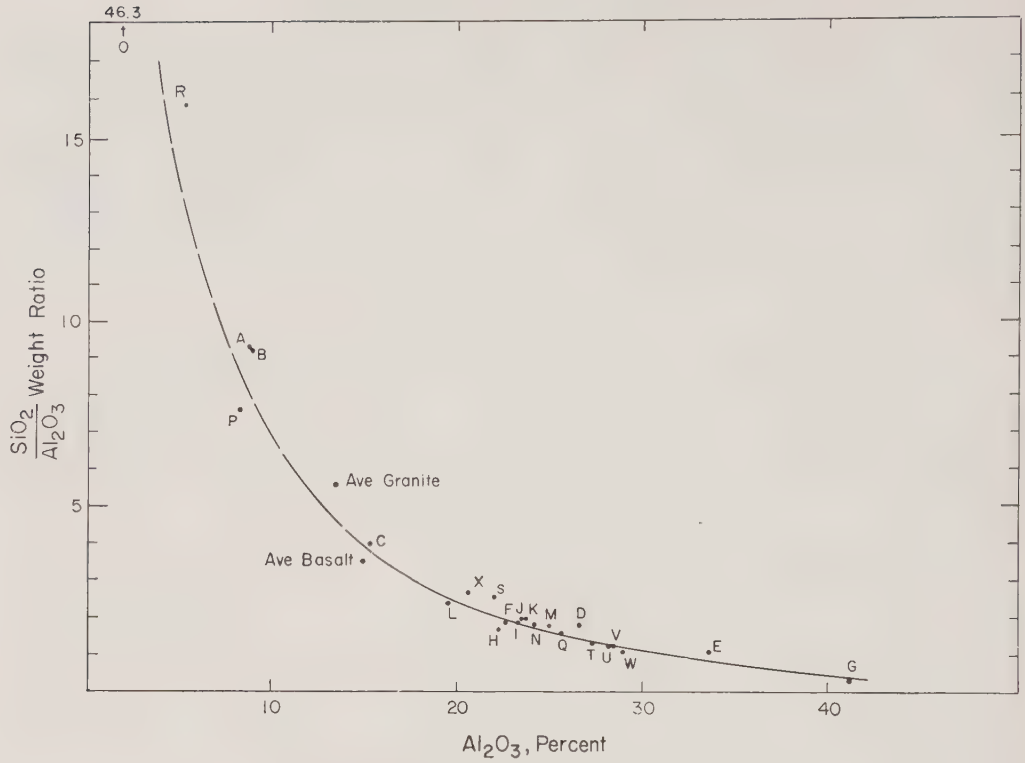

Fig. 1. Silica–alumina ratio as a function of alumina.

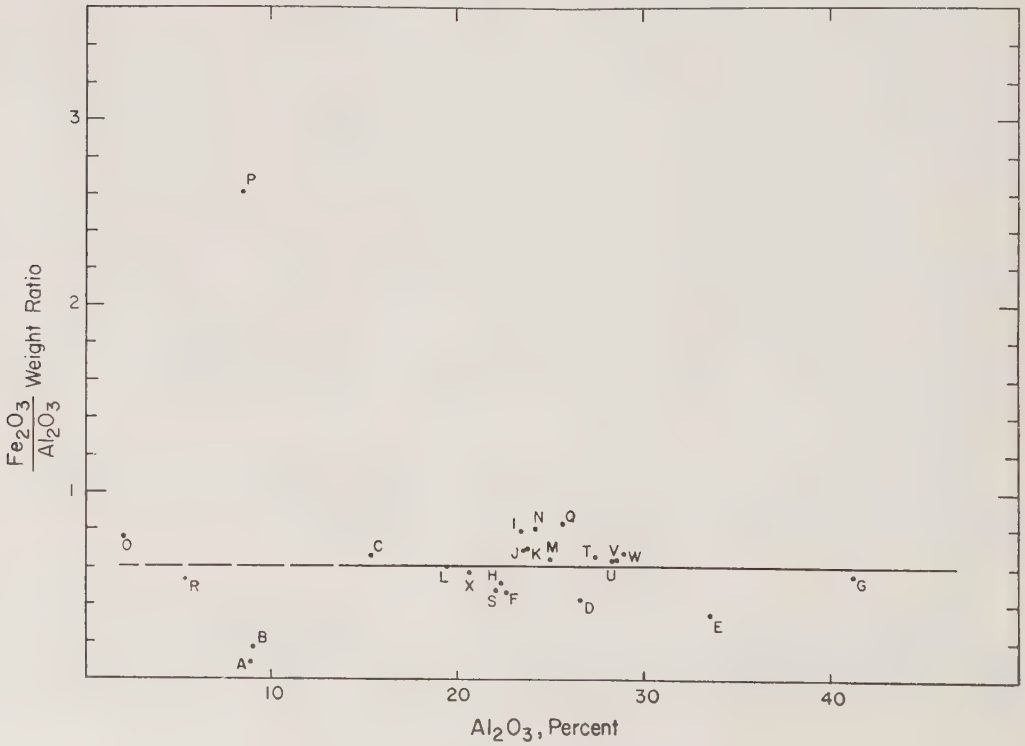

Fig. 2. Ferric oxide–alumina ratio as a function of alumina.

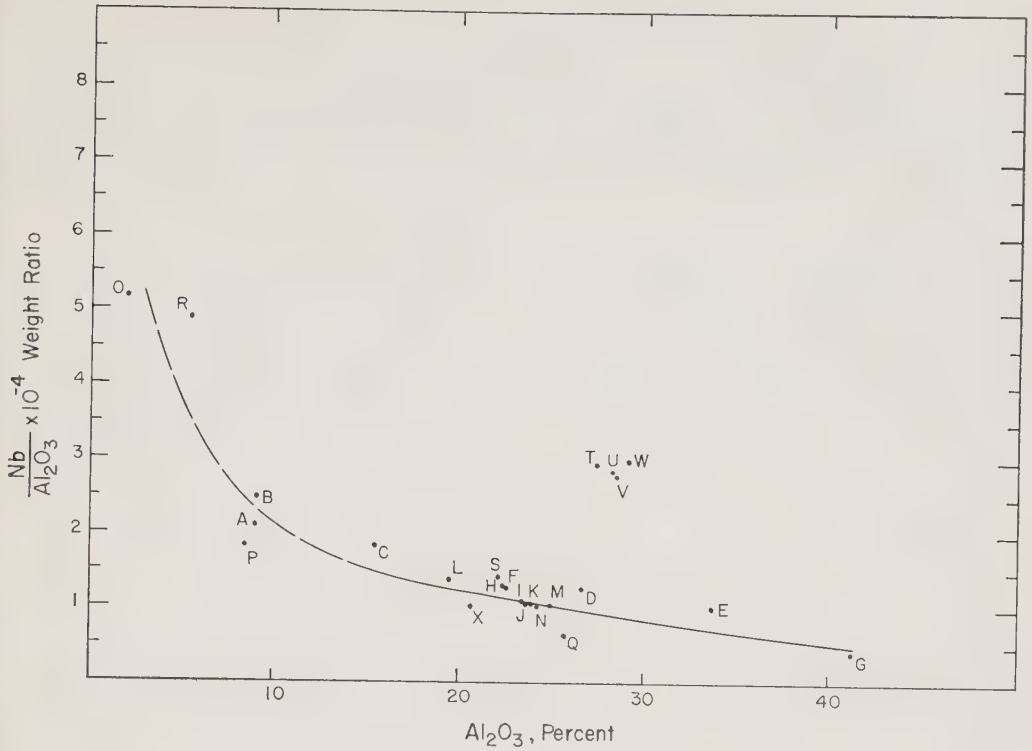

Fig. 3. Niobium–alumina ratio as a function of alumina.

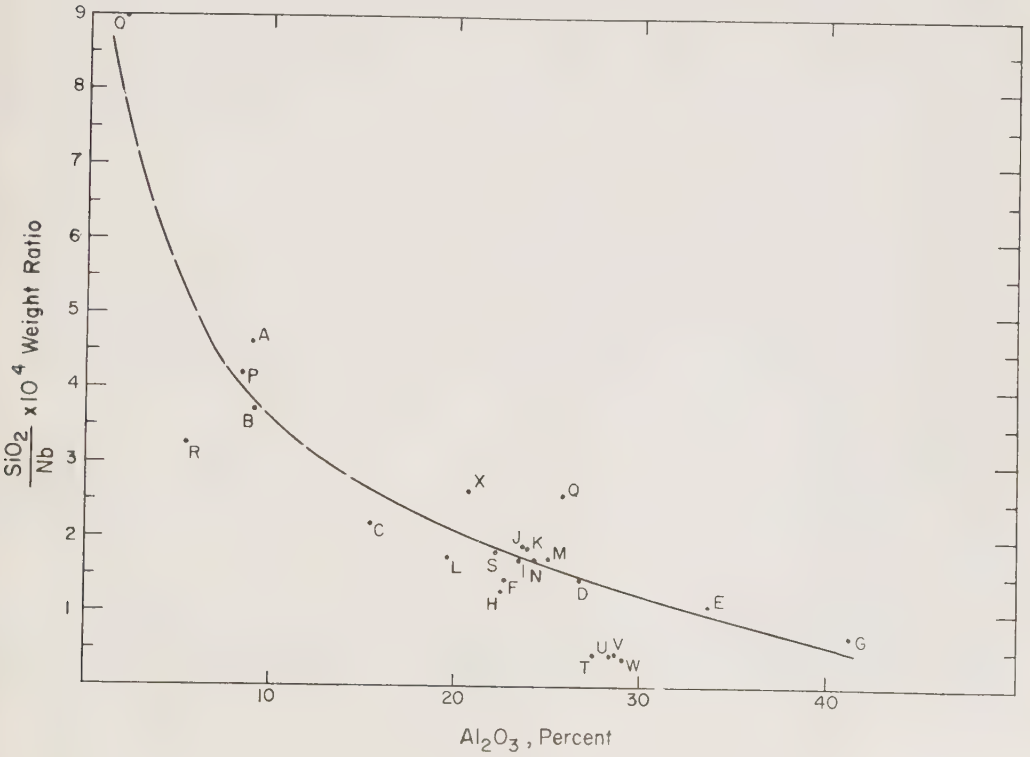

Fig. 4. Silica–niobium ratio as a function of alumina.

remains roughly constant (Fig. 2); the Nb/Al_2O_3 ratio decreases (Fig. 3); and the SiO_2/Nb ratio decreases (Fig. 4). Based on these ratios it is clear that with increase in aluminium Si is being depleted faster than Nb from the soils, and that both Si and Nb are being depleted faster than Al. The depletion sequence for these soils is, therefore:

$$Si > Nb > Al = Fe$$

Because niobium is depleted from the soils to a greater extent than aluminium, any concentration of aluminium during the formation of a soil will be accompanied by a smaller concentration of niobium. This, of course, represents a gross chemical pattern to be expected during the development of such soils, but does not eliminate the possibility that chemical processes accompanying the degradation of a parent rock during the formation of a lateritic soil may be accompanied by localized niobium–aluminium interrelationships that do not follow the above depletion sequence.

The excellent consistency of niobium with aluminium and silicon for most of the samples studied in this work, as shown in Figs. 3 and 4, indicates that the source materials from which these soils developed must have contained no unusual concentrations of niobium. Only the Nigerian samples deviate appreciably from the smooth curves as a result of their unusually high niobium contents. It seems that development of soils with high niobium content is dependent upon their origin from sources with high niobium content. The high niobium content of bauxites, from Arkansas (about 500 p.p.m.) is, in this respect, probably related to the unusually high concentration of the element in the parent nepheline syenite (130 p.p.m.) (Gordon and Murata, 1952). These workers reported a 3·8-fold concentration of niobium in the bauxite compared to that in the nepheline syenite; aluminium on the other hand, was concentrated by a factor of only 2·7. Whether this reversal in concentration factors is peculiar to the nepheline syenite or to the process of bauxite formation is not known.

It was of some interest to inquire as to the form in which niobium occurs in the soils. Rankama (1948) reported four samples of muscovite to contain from about 28 to 230 p.p.m. niobium, and two samples of biotite to contain from about 360 to 1300 p.p.m. niobium. In a more recent paper, Odikadze (1958) reported as much as 350 p.p.m. of niobium in muscovites. The geochemical association of niobium and titanium has also been reported (Fleischer *et al.*, 1952). For example, brookite, rutile and other titanium minerals were shown to contain as much as several per cent niobium.

Samples N-4-1 and CI-5-1 were separated into "sand", "clay" and "heavy minerals in sand"; analyses of the separates are shown in Table 2. A material balance shows clearly that very little of the niobium in these two samples is associated with the separable heavy minerals. X-ray analyses of the "sand" and "clay" fractions failed to show the presence of mica.

An association of niobium and titanium is suggested, but an additional association of niobium with clay minerals is indicated by the Nb/Ti ratio for the "clay" fraction of sample N-4-1. The well-known occurrence of authigenic rutile in clays may in part explain the double association of Nb with Ti and clays.

Conclusions

The niobium content of twenty lateritic soils from West Africa ranges from 10 to 34 p.p.m. and averages 24 p.p.m. This value is similar to that for the abundance of niobium in the lithosphere (20 p.p.m.) and illustrates that little or no concentration of niobium has occurred during the formation of the soils. Four samples of

Table 2. Distribution of niobium in fractions of samples N–4–1 and Cl–5–1

Fraction	N–4–1				Cl–5–1			
	Wt.%	% Nb	% TiO_2	Nb/TiO_2	Wt.%	% Nb	% TiO_2	Nb/TiO_2
"Sand" less "heavy minerals"	15·9	0·0070	4·3	0·0016	37·4	0·0023	1·5	0·0015
"heavy minerals" from "sand"	1·2	0·034	24·5	0·0014	0·2	0·0028	—	—
"Clay"	82·9	0·0078	3·0	0·0026	62·4	0·0028	1·9	0·0015

lateritic soil from Nigeria contain 79 to 87 p.p.m. of niobium, but these soils were taken close to a niobium mining area and were probably derived from non-representative parent rocks.

Comparison of all twenty-four samples with each other has led to the following depletion sequence:

$$Si > Nb > Al = Fe$$

This sequence refers to overall chemical changes that occur in lateritic soils as the aluminium content increases.

Acknowledgements—We are grateful to Dorothy Carroll for carrying out heavy mineral separations and to A. M. Pommer for the X-ray analyses.

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